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(54) Title: IMPROVED METAL-LIGAND COMPLEX CATALYZED PROCESSES

(57) Abstract

This invention relates to a method of stabilizing a metal-organopolyphosphite ligand complex catalyst against deactivation in a process which comprises reacting one or more reactants in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more products, which method comprises conducting said process in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

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IMPROVED METAL-LIGAND COMPLEX CATALYZED PROCESSES

Brief Summary of the Invention

Technical Field

This invention relates to metal-organopolyphosphite ligand complex catalyzed processes. More particularly this invention relates to the use of one or more free heterocyclic nitrogen compounds to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst of such processes.

Background of the Invention

It is well known in the art that aldehydes may be readily produced by reacting an olefinically unsaturated compound with carbon monoxide and hydrogen in the presence of an rhodium-organophosphite ligand complex catalyst and that preferred processes involve continuous hydroformylation and recycling of the catalyst solution such as disclosed, for example, in U.S. Patent Nos. 4,148,830; 4,717,775 and 4,769,498. Such aldehydes have a wide range of known utility and are useful, for example, as intermediates for hydrogenation to aliphatic alcohols, for aldol condensation to produce plasticizers and for oxidation to produce aliphatic acids.

However, notwithstanding the benefits attendant with such rhodium-organophosphite ligand complex catalyzed hydroformylation processes, stabilization of the catalyst and organophosphite ligand remains a primary concern of the art. Obviously catalyst stability is a key issue in the employment of any catalyst. Loss of catalyst or catalytic activity due to undesirable reactions of the highly expensive rhodium catalysts can be detrimental to the production of the desired aldehyde. Likewise degradation of the organophosphite ligand employed during the hydroformylation process

can lead to poisoning organophosphite compounds or inhibitors or acidic byproducts that can lower the catalytic activity of the rhodium catalyst or increase the rate of organophosphorus ligand loss. Moreover, production costs of the aldehyde product obviously increase when productivity of the catalyst decreases.

Numerous methods have been proposed to maintain catalyst and/or organophosphite ligand stability. For instance, U.S. Patent No. 5,288,918 suggests employing a catalytic activity enhancing additive such as water and/or a weakly acidic compound; U.S. Patent No. 5,364,950 suggests adding an epoxide to stabilize the organophosphite ligand; and U.S. Patent No. 4,774,361 suggests carrying out the vaporization separation employed to recover the aldehyde product from the catalyst in the presence of an organic polymer containing polar functional groups selected from the class consisting of amide, ketone, carbamate, urea, and carbonate radicals in order to prevent and/or lessen rhodium precipitation from solution as rhodium metal or in the form of clusters of rhodium. Notwithstanding the value of the teachings of said references, the search for alternative methods and hopefully an even better and more efficient means for stabilizing the rhodium catalyst and organophosphite ligand employed remains an ongoing activity in the art.

For instance, while the suggested use of organopolyphosphite promoted rhodium hydroformylation catalysts is well known in the art as seen, for example, by said U.S. Patent No. 4,769,498, the activity of such catalysts has been found to decrease at a slow, but appreciable rate over the course of the continuous liquid recycle hydroformylation process.

This loss in catalytic activity of the organopolyphosphite promoted rhodium hydroformylation catalyst is believed to be due in part to the low carbon monoxide partial pressure present during, for example, in the vaporization employed in the separation and recovery of the aldehyde product from the reaction product mixture. When

using a vaporizer to facilitate separation of the aldehyde product of the process, a harsh environment of a high temperature and a low carbon monoxide partial pressure than employed during hydroformylation is created, and it has been found that when a organopolyphosphite promoted rhodium catalyst is placed under such vaporizer conditions, it will deactivate at an accelerated pace with time. It is further believed that this deactivation is likely caused by the formation of an inactive or less active rhodium species. Such is especially evident when the carbon monoxide partial pressure is very low or absent. It has also been observed that the rhodium becomes susceptible to precipitation under prolonged exposure to such vaporizer conditions.

For instance, it is theorized that under harsh conditions such as exist in a vaporizer, the active catalyst, which under hydroformylation conditions is believed to comprise a complex of rhodium, organopolyphosphite, carbon monoxide and hydrogen, loses at least some of its coordinated carbon monoxide, thereby providing a route for the formation of such a catalytically inactive or less active rhodium species.

Two potential routes for the formation of such an inactive or less catalytically active rhodium species, which may theoretically serve to explain the decline in catalytic activity that is experienced over the course of time of a rhodium-organopolyphosphite ligand complex catalyzed hydroformylation process, involve the replacement of said lost carbon monoxide with an additional organopolyphosphite ligand to form rhodium-bis(organopolyphosphite) complexes or the formation of rhodium complex clusters that may be produced by polymerization of a rhodium-organopolyphosphite ligand complex formed as a result of said lost carbon monoxide. Moreover such inactive or less active formed rhodium complexes may be susceptible to precipitation from solution due to their poorer solubility in the hydroformylation reaction medium than that of the active rhodium catalyst. Accordingly, a successful method for preventing and/or

lessening such deactivation of the catalyst would be highly desirable to the art.

Disclosure of the Invention

It has been discovered that certain free heterocyclic nitrogen compounds may be employed to effectively prevent and/or lessen deactivation of metal-organopolyphosphite ligand complex catalysts that may occur over the course of time during processes, e.g., a hydroformylation process directed to producing one or more aldehydes in which at least a portion of said hydroformylation process is conducted under harsh conditions such as exist in a vaporizer, for example, a continuous liquid recycle hydroformylation process in which separation of the aldehyde product from the hydroformylation reaction product fluid occurs under conditions of low carbon monoxide partial pressure.

This invention relates to a method of stabilizing a metal-organopolyphosphite ligand complex catalyst against deactivation in a process which comprises reacting one or more reactants in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more products, which method comprises conducting said process in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

This invention also relates in part to a method of stabilizing a metal-organopolyphosphite ligand complex catalyst against deactivation in a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, which method comprises conducting

said hydroformylation process in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

This invention further relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, and in which at least a portion of said hydroformylation process is conducted under conditions sufficient to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, wherein said hydroformylation process is conducted in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

This invention yet further relates to a continuous liquid recycle hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, and in which at least a portion of said process is conducted under vaporization separation conditions sufficient to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, wherein said process is conducted in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

This invention also relates in part to an improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free

organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, and wherein at least a portion of said process is conducted at a carbon monoxide partial pressure sufficiently low to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, the improvement comprising conducting said process in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

This invention further relates to an improved continuous liquid recycle hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone by vaporization separation the one or more aldehydes from said reaction product fluid, and wherein said vaporization separation is conducted at a carbon monoxide partial pressure sufficiently low to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, the improvement comprising conducting said vaporization separation in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

Detailed Description

The hydroformylation processes of this invention may be asymmetric or non-asymmetric, the preferred processes being non-asymmetric, and may be conducted in any continuous or semi-continuous fashion and may involve any catalyst liquid and/or gas

recycle operation desired. Thus it should be clear that the particular hydroformylation process for producing such aldehydes from an olefinic unsaturated compound, as well as the reaction conditions and ingredients of the hydroformylation process are not critical features of this invention. As used herein, the term "hydroformylation" is contemplated to include, but not limited to, all permissible asymmetric and non-asymmetric hydroformylation processes which involve converting one or more substituted or unsubstituted olefinic compounds or a reaction mixture comprising one or more substituted or unsubstituted olefinic compounds to one or more substituted or unsubstituted aldehydes or a reaction mixture comprising one or more substituted or unsubstituted aldehydes. As used herein, the term "reaction product fluid" is contemplated to include, but not limited to, a reaction mixture containing an amount of any one or more of the following: (a) a metal-organopolyphosphite ligand complex catalyst, (b) free organopolyphosphite ligand, (c) one or more phosphorus acidic compounds formed in the reaction, (d) aldehyde product formed in the reaction, (e) unreacted reactants, and (f) an organic solubilizing agent for said metal-organopolyphosphite ligand complex catalyst and said free organopolyphosphite ligand. The reaction product fluid encompasses, but is not limited to, (a) the reaction medium in the reaction zone, (b) the reaction medium stream on its way to the separation zone, (c) the reaction medium in the separation zone, (d) the recycle stream between the separation zone and the reaction zone, (e) the reaction medium withdrawn from the reaction zone or separation zone for treatment in the acid removal zone, (f) the withdrawn reaction medium treated in the acid removal zone, (g) the treated reaction medium returned to the reaction zone or separation zone, and (h) reaction medium in external cooler.

Illustrative metal-organopolyphosphite ligand complex catalyzed hydroformylation processes which may experience such hydrolytic degradation of the organopolyphosphite ligand and catalytic

deactivation include such processes as described, for example, in U.S. Patent Nos. 4,148,830; 4,593,127; 4,769,498; 4,717,775; 4,774,361; 4,885,401; 5,264,616; 5,288,918; 5,360,938; 5,364,950; and 5,491,266; the disclosures of which are incorporated herein by reference. Accordingly, the hydroformylation processing techniques of this invention may correspond to any known processing techniques. Preferred processes are those involving catalyst liquid recycle hydroformylation processes.

In general, such catalyst liquid recycle hydroformylation processes involve the production of aldehydes by reacting an olefinic unsaturated compound with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst in a liquid medium that also contains an organic solvent for the catalyst and ligand. Preferably free organopolyphosphite ligand is also present in the liquid hydroformylation reaction medium. By "free organopolyphosphite ligand" is meant organopolyphosphite ligand that is not complexed with (tied to or bound to) the metal, e.g., metal atom, of the complex catalyst. The recycle procedure generally involves withdrawing a portion of the liquid reaction medium containing the catalyst and aldehyde product from the hydroformylation reactor (i.e., reaction zone), either continuously or intermittently, and recovering the aldehyde product therefrom by use of a composite membrane such as disclosed in U.S. Patent No. 5,430,194 and copending U.S. Patent Application Serial No. 08/430,790, filed May 5,1995, the disclosures of which are incorporated herein by reference, or by the more conventional and preferred method of distilling it (i.e., vaporization separation) in one or more stages under normal, reduced or elevated pressure, as appropriate, in a separate distillation zone, the non-volatilized metal catalyst containing residue being recycled to the reaction zone as disclosed, for example, in U.S. Patent No. 5,288,918. Condensation of the volatilized materials, and separation and further recovery thereof, e.g., by further distillation, can be carried out in any

conventional manner, the crude aldehyde product can be passed on for further purification and isomer separation, if desired, and any recovered reactants, e.g., olefinic starting material and syn gas, can be recycled in any desired manner to the hydroformylation zone (reactor). The recovered metal catalyst containing raffinate of such membrane separation or recovered non-volatilized metal catalyst containing residue of such vaporization separation can be recycled, to the hydroformylation zone (reactor) in any conventional manner desired.

In a preferred embodiment, the hydroformylation reaction product fluids employable herein includes any fluid derived from any corresponding hydroformylation process that contains at least some amount of four different main ingredients or components, i.e., the aldehyde product, a metal-organopolyphosphite ligand complex catalyst, free organopolyphosphite ligand and an organic solubilizing agent for said catalyst and said free ligand, said ingredients corresponding to those employed and/or produced by the hydroformylation process from whence the hydroformylation reaction mixture starting material may be derived. It is to be understood that the hydroformylation reaction mixture compositions employable herein can and normally will contain minor amounts of additional ingredients such as those which have either been deliberately employed in the hydroformylation process or formed in situ during said process. Examples of such ingredients that can also be present include unreacted olefin starting material, carbon monoxide and hydrogen gases, and in situ formed type products, such as saturated hydrocarbons and/or unreacted isomerized olefins corresponding to the olefin starting materials, and high boiling liquid aldehyde condensation byproducts, as well as other inert co-solvent type materials or hydrocarbon additives, if employed.

Illustrative metal-organopolyphosphite ligand complex catalysts employable in such hydroformylation reactions encompassed by this invention as well as methods for their preparation are well

known in the art and include those disclosed in the above mentioned patents. In general such catalysts may be preformed or formed in situ as described in such references and consist essentially of metal in complex combination with an organopolyphosphite ligand. It is believed that carbon monoxide is also present and complexed with the metal in the active species. The active species may also contain hydrogen directly bonded to the metal.

The catalyst useful in the hydroformylation process includes a metal-organopolyphosphite ligand complex catalyst which can be optically active or non-optically active. The permissible metals which make up the metal-organopolyphosphite ligand complexes include Group 8, 9 and 10 metals selected from rhodium (Rh), cobalt (Co), iridium (Ir), ruthenium (Ru), iron (Fe), nickel (Ni), palladium (Pd), platinum (Pt), osmium (Os) and mixtures thereof, with the preferred metals being rhodium, cobalt, iridium and ruthenium, more preferably rhodium, cobalt and ruthenium, especially rhodium. Other permissible metals include Group 6 metals selected from chromium (Cr), molybdenum (Mo), tungsten (W) and mixtures thereof. Mixtures of metals from Groups 6, 8, 9 and 10 may also be used in this invention. The permissible organopolyphosphite ligands which make up the metal-organopolyphosphite ligand complexes and free organopolyphosphite ligand include mono-, di-, tri- and higher polyorganophosphites. Mixtures of such ligands may be employed if desired in the metal-organopolyphosphite ligand complex catalyst and/or free ligand and such mixtures may be the same or different. This invention is not intended to be limited in any manner by the permissible organopolyphosphite ligands or mixtures thereof. It is to be noted that the successful practice of this invention does not depend and is not predicated on the exact structure of the metal-organopolyphosphite ligand complex species, which may be present in their mononuclear, dinuclear and/or higher nuclearity forms. Indeed, the exact structure is not known. Although it is not intended herein to

be bound to any theory or mechanistic discourse, it appears that the catalytic species may in its simplest form consist essentially of the metal in complex combination with the organopolyphosphite ligand and carbon monoxide and/or hydrogen when used.

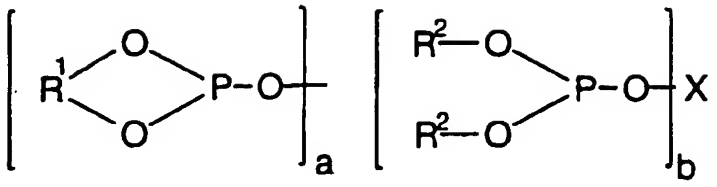
The term "complex" as used herein and in the claims means a coordination compound formed by the union of one or more electronically rich molecules or atoms capable of independent existence with one or more electronically poor molecules or atoms, each of which is also capable of independent existence. For example, the organopolyphosphite ligands employable herein may possess one or more phosphorus donor atoms, each having one available or unshared pair of electrons which are each capable of forming a coordinate covalent bond independently or possibly in concert (e.g., via chelation) with the metal. Carbon monoxide (which is also properly classified as a ligand) can also be present and complexed with the metal. The ultimate composition of the complex catalyst may also contain an additional ligand, e.g., hydrogen or an anion satisfying the coordination sites or nuclear charge of the metal. Illustrative additional ligands include, for example, halogen (Cl, Br, I), alkyl, aryl, substituted aryl, acyl, CF_3, C_2F_5, CN, $(R)_2PO$ and $RP(O)(OH)O$ (wherein each R is the same or different and is a substituted or unsubstituted hydrocarbon radical, e.g., the alkyl or aryl), acetate, acetylacetonate, SO_4, PF_4, PF_6, NO_2, NO_3, CH_3O, $CH_2=CHCH_2$, $CH_3CH=CHCH_2$, C_6H_5CN, CH_3CN, NH_3, pyridine, $(C_2H_5)_3N$, mono-olefins, diolefins and triolefins, tetrahydrofuran, and the like. It is of course to be understood that the complex species are preferably free of any additional organic ligand or anion that might poison the catalyst or have an undue adverse effect on catalyst performance. It is preferred in the metal-organopolyphosphite ligand complex catalyzed hydroformylation reactions that the active catalysts be free of halogen and sulfur directly bonded to the metal, although such may not be absolutely necessary.

The number of available coordination sites on such metals is well known in the art. Thus the catalytic species may comprise a complex catalyst mixture, in their monomeric, dimeric or higher nuclearity forms, which are preferably characterized by at least one organopolyphosphite-containing molecule complexed per one molecule of metal, e.g., rhodium. For instance, it is considered that the catalytic species of the preferred catalyst employed in a hydroformylation reaction may be complexed with carbon monoxide and hydrogen in addition to the organopolyphosphite ligands in view of the carbon monoxide and hydrogen gas employed by the hydroformylation reaction.

The organopolyphosphites that may serve as the ligand of the metal-organopolyphosphite ligand complex catalyst and/or free ligand of the hydroformylation processes and reaction product fluids of this invention may be of the achiral (optically inactive) or chiral (optically active) type and are well known in the art. Achiral organopolyphosphites are preferred.

Among the organopolyphosphites that may serve as the ligand of the metal-organopolyphosphite ligand complex catalyst containing reaction product fluids of this invention and/or any free organopolyphosphite ligand of the hydroformylation process that might also be present in said reaction product fluids are organopolyphosphite compounds described below. Such organopolyphosphite ligands employable in this invention and/or methods for their preparation are well known in the art.

Representative organopolyphosphites contain two or more tertiary (trivalent) phosphorus atoms and may include those having the formula:



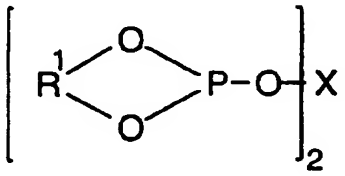
(I)

wherein X represents a substituted or unsubstituted n-valent organic bridging radical containing from 2 to 40 carbon atoms, each R^1 is the same or different and represents a divalent organic radical containing from 4 to 40 carbon atoms, each R^2 is the same or different and represents a substituted or unsubstituted monovalent hydrocarbon radical containing from 1 to 24 carbon atoms, a and b can be the same or different and each have a value of 0 to 6, with the proviso that the sum of a + b is 2 to 6 and n equals a + b. Of course it is to be understood that when a has a value of 2 or more, each R^1 radical may be the same or different, and when b has a value of 1 or more, each R^2 radical may be the same or different.

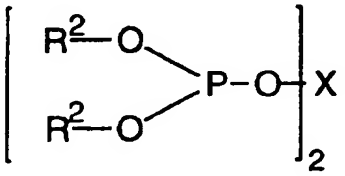
Representative n-valent (preferably divalent) hydrocarbon bridging radicals represented by X and representative divalent organic radicals represented by R^1 above, include both acyclic radicals and aromatic radicals, such as alkylene, alkylene-Q_m-alkylene, cycloalkylene, arylene, bisarylene, arylene-alkylene, and arylene-$(CH_2)_y$-Q_m-$(CH_2)_y$-arylene radicals, and the like, wherein each y is the same or different and is a value of 0 or 1, Q represents a divalent bridging group selected from -$C(R^3)_2$-, -O-, -S-, -NR^4-, $Si(R^5)_2$- and -CO-, wherein each R^3 is the same or different and represents hydrogen, an alkyl radical having from 1 to 12 carbon atoms, phenyl, tolyl, and anisyl, R^4 represents hydrogen or a substituted or unsubstituted monovalent hydrocarbon radical, e.g., an alkyl radical having 1 to 4 carbon atoms; each R^5 is the same or different and represents hydrogen or an alkyl radical, and m is a value of 0 or 1. The more preferred acyclic radicals represented by X and R^1 above are

divalent alkylene radicals, while the more preferred aromatic radicals represented by X and R^1 above are divalent arylene and bisarylene radicals, such as disclosed more fully, for example, in U.S. Patent Nos. 4,769,498; 4,774,361: 4,885,401; 5,179,055; 5,113,022; 5,202,297; 5,235,113; 5,264,616 and 5,364,950, and European Patent Application Publication No. 662,468, and the like, the disclosures of which are incorporated herein by reference. Representative preferred monovalent hydrocarbon radicals represented by each R^2 radical above include alkyl and aromatic radicals.

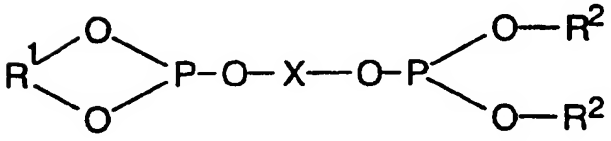
Illustrative preferred organopolyphosphites may include bisphosphites such as those of Formulas (II) to (IV) below:



(II)



(III)

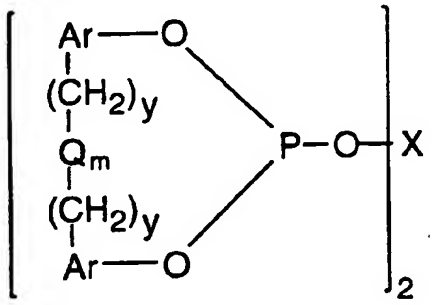


(IV)

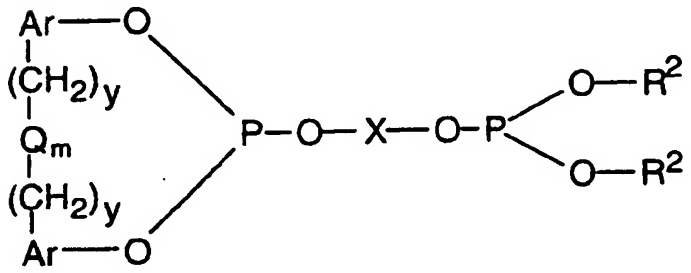
wherein each R^1 , R^2 and X of Formulas (II) to (IV) are the same as defined above for Formula (I). Preferably each R^1 and X represents a divalent hydrocarbon radical selected from alkylene, arylene, arylene-alkylene-arylene, and bisarylene, while each R^2 radical represents a

monovalent hydrocarbon radical selected from alkyl and aryl radicals. Organopolyphosphite ligands of such Formulas (II) to (IV) may be found disclosed, for example, in U.S. Patent Nos. 4,668,651; 4,748,261; 4,769,498; 4,774,361; 4,885,401; 5,113,022; 5,179,055; 5,202,297; 5,235,113; 5,254,741; 5,264,616; 5,312,996; 5,364,950; and 5,391,801; the disclosures of all of which are incorporated herein by reference.

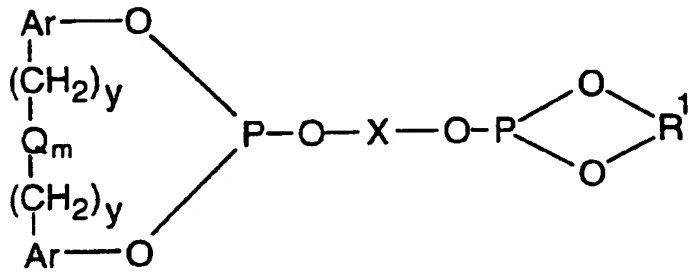
Representative of more preferred classes of organobisphosphites are those of the following Formulas (V) to (VII):



(V)



(VI)



(VII)

wherein Q, R^1, R^2, X , m, and y are as defined above, and each Ar is the same or different and represents a substituted or unsubstituted aryl radical. Most preferably X represents a divalent aryl-$(CH_2)_y$-$(Q)_m$-$(CH_2)_y$-aryl radical wherein each y individually has a value of 0 or 1; m has a value of 0 or 1 and Q is -O-, -S- or -$C(R^3)_2$ where each R^3 is the same or different and represents hydrogen or a methyl radical. More preferably each alkyl radical of the above defined R^2 groups may contain from 1 to 24 carbon atoms and each aryl radical of the above-defined Ar, X, R^1 and R^2 groups of the above Formulas (V) to (VII) may contain from 6 to 18 carbon atoms and said radicals may be the same or different, while the preferred alkylene radicals of X may contain from 2 to 18 carbon atoms and the preferred alkylene radicals of R^1 may contain from 5 to 18 carbon atoms. In addition, preferably the divalent Ar radicals and divalent aryl radicals of X of the above formulas are phenylene radicals in which the bridging group represented by –$(CH_2)_y$–$(Q)_m$–$(CH_2)_y$– is bonded to said phenylene radicals in positions that are ortho to the oxygen atoms of the formulas that connect the phenylene radicals to their phosphorus atom of the formulae. It is also preferred that any substituent radical when present on such phenylene radicals be bonded in the para and/or ortho position of the phenylene radicals in relation to the oxygen atom that bonds the given substituted phenylene radical to its phosphorus atom.

Moreover, if desired any given organopolyphosphite in the above Formulas (I) to (VII) may be an ionic phosphite, i.e., may contain one or more ionic moieties selected from the group consisting of:

- — SO_3M wherein M represents inorganic or organic cation,
- — PO_3M wherein M represents inorganic or organic cation,
- — $N(R^6)_3X^1$ wherein each R^6 is the same or different and represents a hydrocarbon radical containing from 1 to 30 carbon atoms, e.g., alkyl, aryl, alkaryl, aralkyl, and

cycloalkyl radicals, and X^1 represents inorganic or organic anion,

— CO_2M wherein M represents inorganic or organic cation,

as described, for example, in U.S. Patent Nos. 5,059,710; 5,113,022 5,114,473; 5,449,653; and European Patent Application Publication No. 435,084, the disclosures of which are incorporated herein by reference. Thus, if desired, such organopolyphosphite ligands may contain from 1 to 3 such ionic moieties, while it is preferred that only one such ionic moiety be substituted on any given aryl moiety in the organopolyphosphite ligand when the ligand contains more than one such ionic moiety. As suitable counter-ions, M and X^1, for the anionic moieties of the ionic organopolyphosphites there can be mentioned hydrogen (i.e. a proton), the cations of the alkali and alkaline earth metals, e.g., lithium, sodium, potassium, cesium, rubidium, calcium, barium, magnesium and strontium, the ammonium cation and quaternary ammonium cations, phosphonium cations, arsonium cations and iminium cations. Suitable anionic atoms of radicals include, for example, sulfate, carbonate, phosphate, chloride, acetate, oxalate and the like.

Of course any of the R^1, R^2, X, Q and Ar radicals of such non-ionic and ionic organopolyphosphites of Formulas (I) to (VII) above may be substituted if desired, with any suitable substituent containing from 1 to 30 carbon atoms that does not unduly adversely affect the desired result of the process of this invention. Substituents that may be on said radicals in addition of course to corresponding hydrocarbon radicals such as alkyl, aryl, aralkyl, alkaryl and cyclohexyl substituents, may include for example silyl radicals such as $-Si(R^7)_3$; amino radicals such as $-N(R^7)_2$; phosphine radicals such as -aryl-$P(R^7)_2$; acyl radicals such as $-C(O)R^7$ acyloxy radicals such as $-OC(O)R^7$; amido radicals such as $-CON(R^7)_2$ and $-N(R^7)COR^7$; sulfonyl radicals such as $-SO_2R^7$, alkoxy radicals such as $-OR^7$;

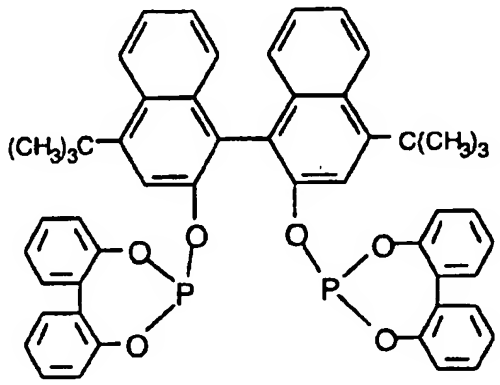
sulfinyl radicals such as -SOR^7, sulfenyl radicals such as -SR^7, phosphonyl radicals such as -$P(O)(R^7)_2$, as well as halogen, nitro, cyano, trifluoromethyl, hydroxy radicals, and the like, wherein each R^7 radical individually represents the same or different monovalent hydrocarbon radical having from 1 to 18 carbon atoms (e.g., alkyl, aryl, aralkyl, alkaryl and cyclohexyl radicals), with the proviso that in amino substituents such as -$N(R^7)_2$ each R^7 taken together can also represent a divalent bridging group that forms a heterocyclic radical with the nitrogen atom, and in amido substituents such as -$C(O)N(R^7)_2$ and -$N(R^7)COR^7$ each R^7 bonded to N can also be hydrogen. Of course it is to be understood that any of the substituted or unsubstituted hydrocarbon radicals groups that make up a particular given organopolyphosphite may be the same or different.

More specifically illustrative substituents include primary, secondary and tertiary alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, neo-pentyl, n-hexyl, amyl, sec-amyl, t-amyl, iso-octyl, decyl, octadecyl, and the like; aryl radicals such as phenyl, naphthyl and the like; aralkyl radicals such as benzyl, phenylethyl, triphenylmethyl, and the like; alkaryl radicals such as tolyl, xylyl, and the like; alicyclic radicals such as cyclopentyl, cyclohexyl, 1-methylcyclohexyl, cyclooctyl, cyclohexylethyl, and the like; alkoxy radicals such as methoxy, ethoxy, propoxy, t-butoxy, -$OCH_2CH_2OCH_3$, -$O(CH_2CH_2)_2OCH_3$, -$O(CH_2CH_2)_3OCH_3$, and the like; aryloxy radicals such as phenoxy and the like; as well as silyl radicals such as -$Si(CH_3)_3$, -$Si(OCH_3)_3$, -$Si(C_3H_7)_3$, and the like; amino radicals such as -NH_2, -$N(CH_3)_2$, -$NHCH_3$, -$NH(C_2H_5)$, and the like; arylphosphine radicals such as -$P(C_6H_5)_2$, and the like; acyl radicals such as -$C(O)CH_3$, -$C(O)C_2H_5$, -$C(O)C_6H_5$, and the like; carbonyloxy radicals such as -$C(O)OCH_3$ and the like; oxycarbonyl radicals such as -$O(CO)C_6H_5$, and the like; amido radicals such as -$CONH_2$, -$CON(CH_3)_2$, -$NHC(O)CH_3$, and the like; sulfonyl radicals

such as $-S(O)_2C_2H_5$ and the like; sulfinyl radicals such as $-S(O)CH_3$ and the like; sulfenyl radicals such as $-SCH_3$, $-SC_2H_5$, $-SC_6H_5$, and the like; phosphonyl radicals such as $-P(O)(C_6H_5)_2$, $-P(O)(CH_3)_2$, $-P(O)(C_2H_5)_2$, $-P(O)(C_3H_7)_2$, $-P(O)(C_4H_9)_2$, $-P(O)(C_6H_{13})_2$, $-P(O)CH_3(C_6H_5)$, $-P(O)(H)(C_6H_5)$, and the like.

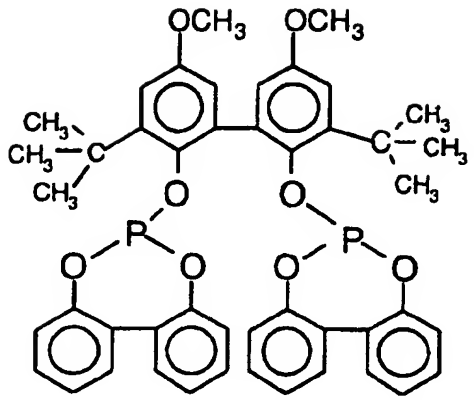
Specific illustrative examples of such organobisphosphite ligands include the following;

6,6'-[[4,4'-bis(1,1-dimethylethyl)-[1,1'-binaphthyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]-dioxaphosphepin having the formula:



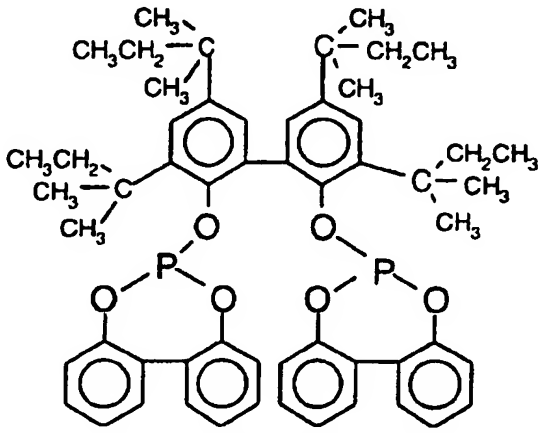
Ligand A

6,6'-[[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



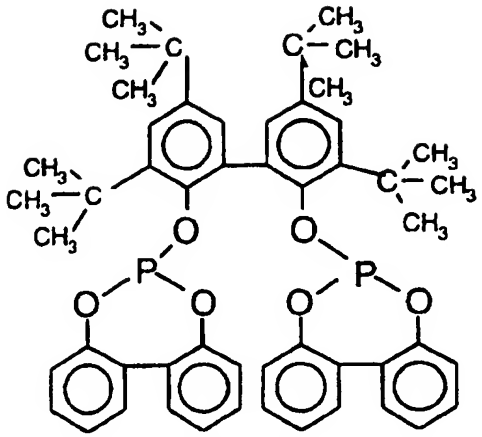
Ligand B

6,6'-[[3,3',5,5'-tetrakis(1,1-dimethylpropyl)-[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



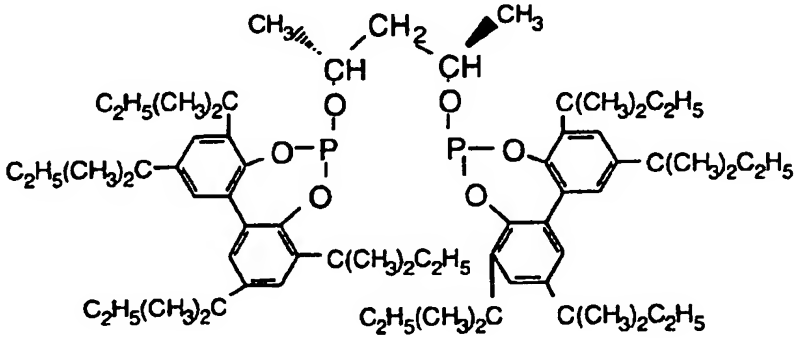
Ligand C

6,6'-[[3,3',5,5'-tetrakis(1,1-dimethylethyl)-[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]-dioxaphosphepin having the formula:



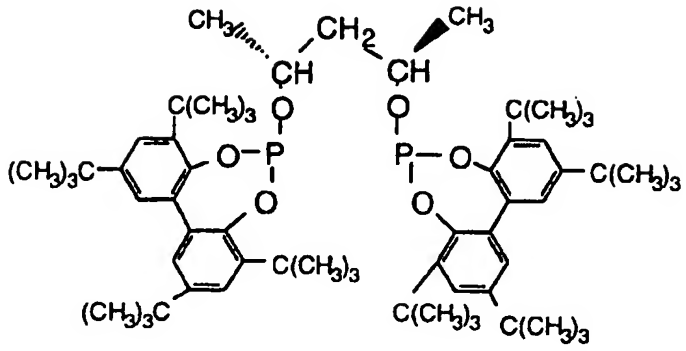
Ligand D

(2R,4R)-di[2,2'-(3,3',5,5'-tetrakis-tert-amyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



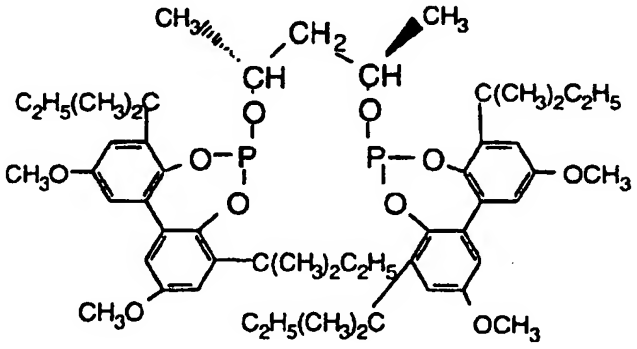
Ligand E

(2R,4R)-di[2,2'-(3,3',5,5'-tetrakis-tert-butyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



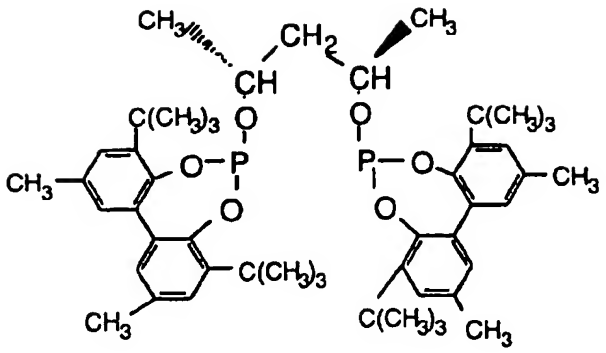
Ligand F

(2R,4R)-di[2,2'-(3,3'-di-amyl-5,5'-dimethoxy-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



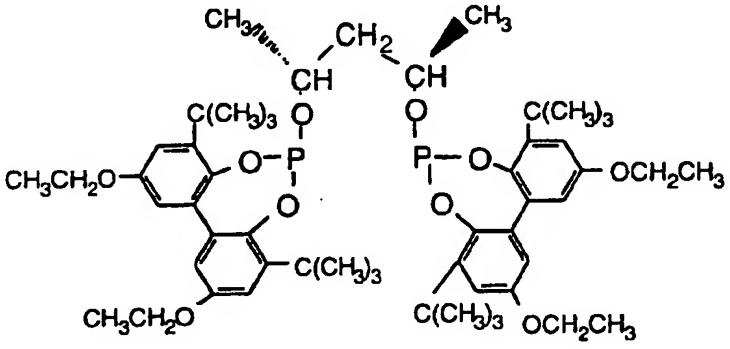
Ligand G

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-dimethyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



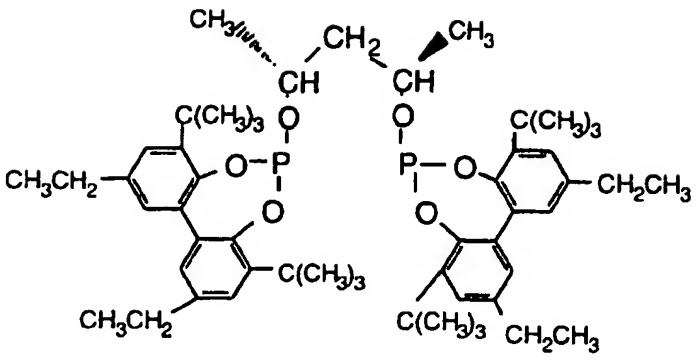
Ligand H

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-diethoxy-1,1'-biphenyl)]- 2,4-pentyldiphosphite having the formula:



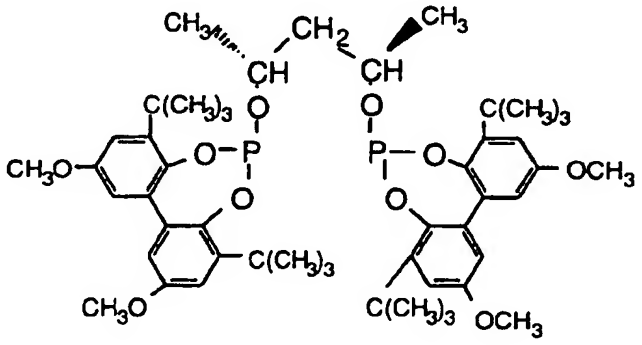
Ligand I

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-diethyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



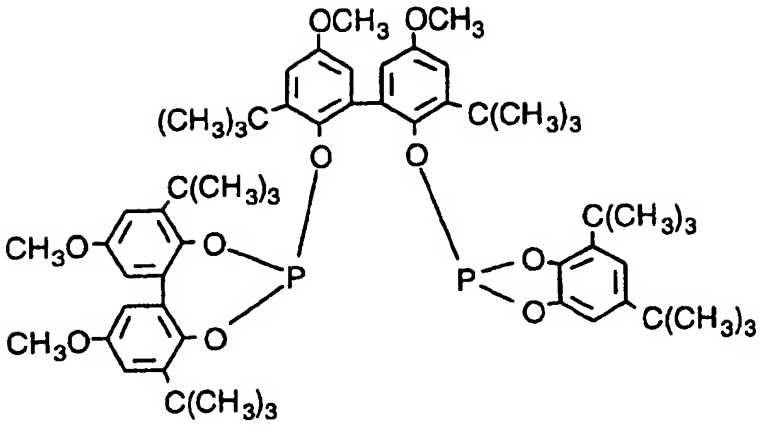
Ligand J

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-dimethoxy-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



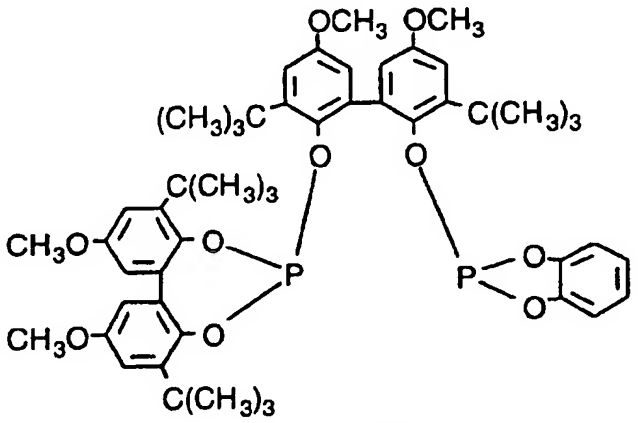
Ligand K

6-[[2'-[(4,6-bis(1,1-dimethylethyl)-1,3,2-benzodioxaphosphol-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



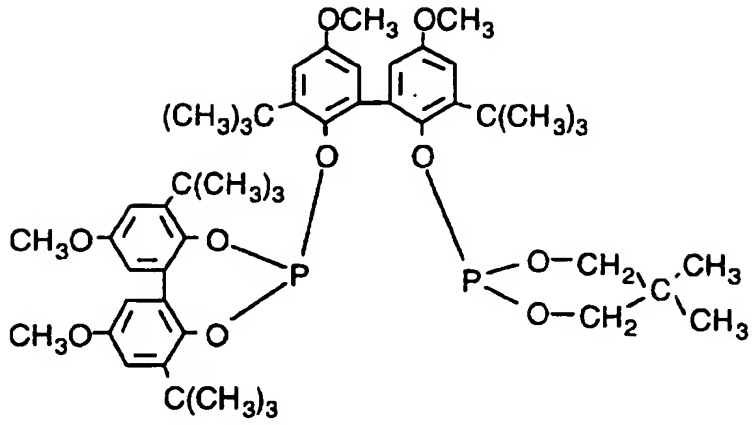
Ligand L

6-[[2'-[1,3,2-benzodioxaphosphol-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



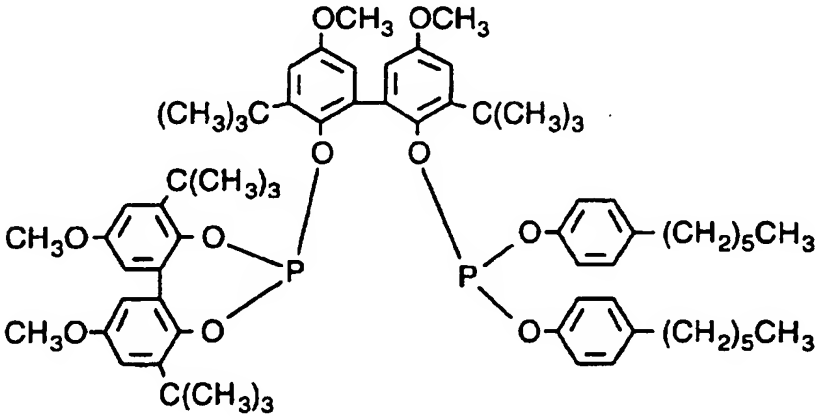
Ligand M

6-[[2'-[(5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



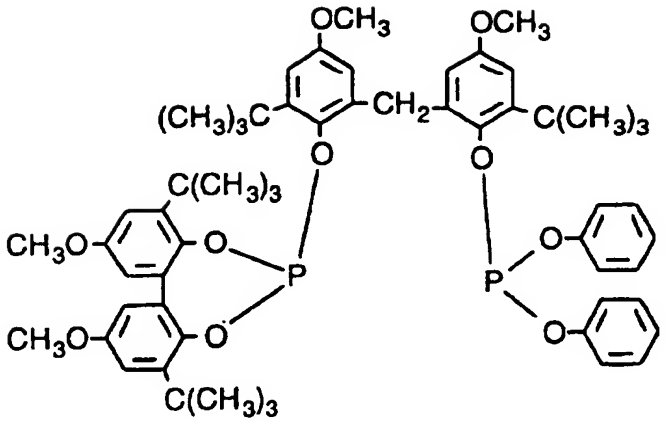
Ligand N

2'-[[4 ,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]-dioxaphosphepin-6-yl]oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'- biphenyl]-2-yl bis(4-hexylphenyl)ester of phosphorous acid having the formula:



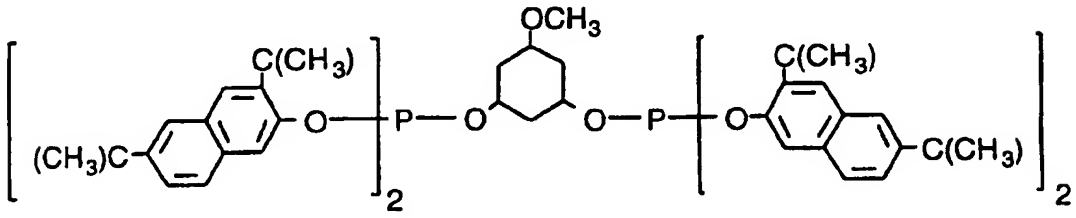
Ligand O

2-[[2-[[4,8,-bis(1,1-dimethylethyl), 2,10-dimethoxydibenzo-[d,f][1,3,2]dioxophosphepin-6-yl]oxy]-3-(1,1-dimethylethyl)-5-methoxyphenyl]methyl]-4-methoxy, 6-(1,1-dimethylethyl)phenyl diphenyl ester of phosphorous acid having the formula:



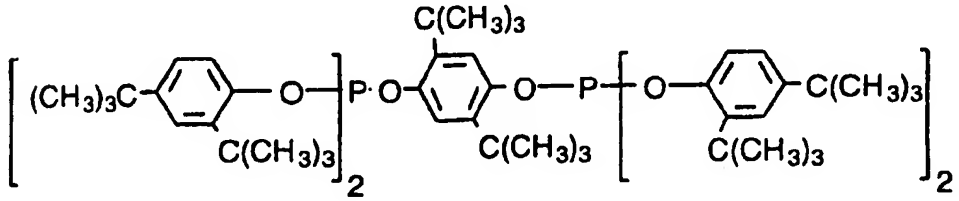
Ligand P

3-methoxy-1,3-cyclohexamethylene tetrakis[3,6-bis(1,1-dimethylethyl)-2-naphthalenyl]ester of phosphorous acid having the formula:



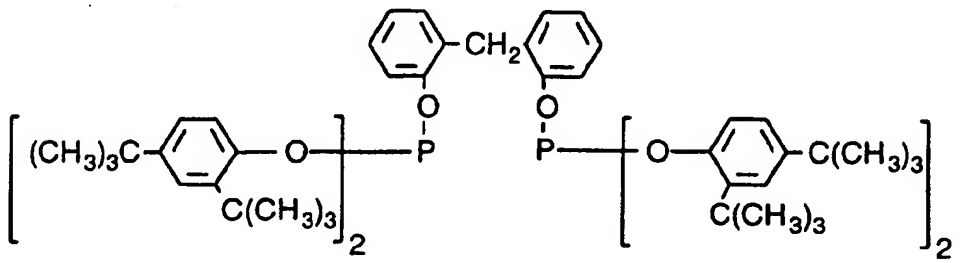
Ligand Q

2,5-bis(1,1-dimethylethyl)-1,4-phenylene tetrakis[2,4-bis(1,1-dimethylethyl)phenyl]ester of phosphorous acid having the formula:



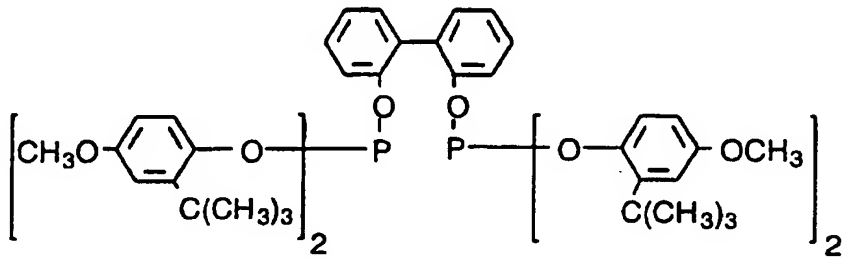
Ligand R

methylenedi-2,1-phenylene tetrakis[2,4-bis(1,1-dimethylethyl)phenyl]ester of phosphorous acid having the formula:



Ligand S

[1,1'-biphenyl]-2,2'-diyl tetrakis[2-(1,1-dimethylethyl)-4-methoxyphenyl]ester of phosphorous acid having the formula:



Ligand T

As noted above, the metal-organopolyphosphite ligand complex catalysts employable in this invention may be formed by methods known in the art. The metal-organopolyphosphite ligand complex catalysts may be in homogeneous or heterogeneous form. For instance, preformed rhodium hydrido-carbonyl-organopolyphosphite ligand catalysts may be prepared and introduced into the reaction mixture of a hydroformylation process. More preferably, the rhodium-organopolyphosphite ligand complex catalysts can be derived from a rhodium catalyst precursor which may be introduced into the reaction

medium for in situ formation of the active catalyst. For example, rhodium catalyst precursors such as rhodium dicarbonyl acetylacetonate, Rh_2O_3, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$ and the like may be introduced into the reaction mixture along with the organopolyphosphite ligand for the in situ formation of the active catalyst. In a preferred embodiment of this invention, rhodium dicarbonyl acetylacetonate is employed as a rhodium precursor and reacted in the presence of a solvent with the organopolyphosphite ligand to form a catalytic rhodium-organopolyphosphite ligand complex precursor which is introduced into the reactor along with excess (free) organopolyphosphite ligand for the in situ formation of the active catalyst. In any event, it is sufficient for the purpose of this invention that carbon monoxide, hydrogen and organopolyphosphite compound are all ligands that are capable of being complexed with the metal and that an active metal-organopolyphosphite ligand catalyst is present in the reaction mixture under the conditions used in the hydroformylation reaction.

More particularly, a catalyst precursor composition can be formed consisting essentially of a solubilized metal-organopolyphosphite ligand complex precursor catalyst, an organic solvent and free organopolyphosphite ligand. Such precursor compositions may be prepared by forming a solution of a rhodium starting material, such as a rhodium oxide, hydride, carbonyl or salt, e.g. a nitrate, which may or may not be in complex combination with a organopolyphosphite ligand as defined herein. Any suitable rhodium starting material may be employed, e.g. rhodium dicarbonyl acetylacetonate, Rh_2O_3, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$, and organopolyphosphite ligand rhodium carbonyl hydrides. Carbonyl and organopolyphosphite ligands, if not already complexed with the initial rhodium, may be complexed to the rhodium either prior to or in situ during the hydroformylation process.

By way of illustration, the preferred catalyst precursor composition of this invention consists essentially of a solubilized rhodium carbonyl organopolyphosphite ligand complex precursor catalyst, a solvent and optionally free organopolyphosphite ligand prepared by forming a solution of rhodium dicarbonyl acetylacetonate, an organic solvent and a organopolyphosphite ligand as defined herein. The organopolyphosphite ligand readily replaces one of the carbonyl ligands of the rhodium acetylacetonate complex precursor at room temperature as witnessed by the evolution of carbon monoxide gas. This substitution reaction may be facilitated by heating the solution if desired. Any suitable organic solvent in which both the rhodium dicarbonyl acetylacetonate complex precursor and rhodium organopolyphosphite ligand complex precursor are soluble can be employed. The amounts of rhodium complex catalyst precursor, organic solvent and organopolyphosphite ligand, as well as their preferred embodiments present in such catalyst precursor compositions may obviously correspond to those amounts employable in the hydroformylation process of this invention. Experience has shown that the acetylacetonate ligand of the precursor catalyst is replaced after the hydroformylation process has begun with a different ligand, e.g., hydrogen, carbon monoxide or organopolyphosphite ligand, to form the active complex catalyst as explained above. The acetylacetone which is freed from the precursor catalyst under hydroformylation conditions is removed from the reaction medium with the product aldehyde and thus is in no way detrimental to the hydroformylation process. The use of such preferred rhodium complex catalytic precursor compositions provides a simple economical and efficient method for handling the rhodium precursor and hydroformylation start-up.

Accordingly, the metal-organopolyphosphite ligand complex catalysts used in the process of this invention consists essentially of the metal complexed with carbon monoxide and a organopolyphosphite ligand, said ligand being bonded (complexed) to

the metal in a chelated and/or non-chelated fashion. Moreover, the terminology "consists essentially of", as used herein, does not exclude, but rather includes, hydrogen complexed with the metal, in addition to carbon monoxide and the organopolyphosphite ligand. Further, such terminology does not exclude the possibility of other organic ligands and/or anions that might also be complexed with the metal. Materials in amounts which unduly adversely poison or unduly deactivate the catalyst are not desirable and so the catalyst most desirably is free of contaminants such as metal-bound halogen (e.g., chlorine, and the like) although such may not be absolutely necessary. The hydrogen and/or carbonyl ligands of an active metal-organopolyphosphite ligand complex catalyst may be present as a result of being ligands bound to a precursor catalyst and/or as a result of in situ formation, e.g., due to the hydrogen and carbon monoxide gases employed in hydroformylation process of this invention.

As noted the hydroformylation processes of this invention involve the use of a metal-organopolyphosphite ligand complex catalyst as described herein. Of course mixtures of such catalysts can also be employed if desired. The amount of metal-organopolyphosphite ligand complex catalyst present in the reaction medium of a given hydroformylation process encompassed by this invention need only be that minimum amount necessary to provide the given metal concentration desired to be employed and which will furnish the basis for at least the catalytic amount of metal necessary to catalyze the particular hydroformylation process involved such as disclosed, for example, in the above-mentioned patents. In general, metal, e.g., rhodium, concentrations in the range of from about 10 parts per million to about 1000 parts per million, calculated as free rhodium, in the hydroformylation reaction medium should be sufficient for most processes, while it is generally preferred to employ from about 10 to 500 parts per million of metal, e.g., rhodium, and more preferably from 25 to 350 parts per million of metal, e.g., rhodium.

In addition to the metal-organopolyphosphite ligand complex catalyst, free organopolyphosphite ligand (i.e., ligand that is not complexed with the metal) may also be present in the hydroformylation reaction medium. The free organopolyphosphite ligand may correspond to any of the above-defined organopolyphosphite ligands discussed above as employable herein. It is preferred that the free organopolyphosphite ligand be the same as the organopolyphosphite ligand of the metal-organopolyphosphite ligand complex catalyst employed. However, such ligands need not be the same in any given process. The hydroformylation process of this invention may involve from about 0.1 moles or less to about 100 moles or higher, of free organopolyphosphite ligand per mole of metal in the hydroformylation reaction medium. Preferably the hydroformylation process of this invention is carried out in the presence of from about 1 to about 50 moles of organopolyphosphite ligand, and more preferably for organopolyphosphites from about 1.1 to about 4 moles of organopolyphosphite ligand, per mole of metal present in the reaction medium; said amounts of organopolyphosphite ligand being the sum of both the amount of organopolyphosphite ligand that is bound (complexed) to the metal present and the amount of free (non-complexed) organopolyphosphite ligand present. Since it is more preferred to produce non-optically active aldehydes by hydroformylating achiral olefins, the more preferred organopolyphosphite ligands are achiral type organopolyphosphite ligands, especially those encompassed by Formula (I) above, and more preferably those of Formulas (II) and (V) above. Of course, if desired, make-up or additional organopolyphosphite ligand can be supplied to the reaction medium of the hydroformylation process at any time and in any suitable manner, e.g. to maintain a predetermined level of free ligand in the reaction medium.

As indicated above, the hydroformylation catalyst may be in heterogeneous form during the reaction and/or during the product

separation. Such catalysts are particularly advantageous in the hydroformylation of olefins to produce high boiling or thermally sensitive aldehydes, so that the catalyst may be separated from the products by filtration or decantation at low temperatures. For example, the rhodium catalyst may be attached to a support so that the catalyst retains its solid form during both the hydroformylation and separation stages, or is soluble in a liquid reaction medium at high temperatures and then is precipitated on cooling.

As an illustration, the rhodium catalyst may be impregnated onto any solid support, such as inorganic oxides, (i.e. alumina, silica, titania, or zirconia) carbon, or ion exchange resins. The catalyst may be supported on, or intercalated inside the pores of, a zeolite, glass or clay; the catalyst may also be dissolved in a liquid film coating the pores of said zeolite or glass. Such zeolite-supported catalysts are particularly advantageous for producing one or more regioisomeric aldehydes in high selectivity, as determined by the pore size of the zeolite. The techniques for supporting catalysts on solids, such as incipient wetness, which will be known to those skilled in the art. The solid catalyst thus formed may still be complexed with one or more of the ligands defined above. Descriptions of such solid catalysts may be found in for example: J. Mol. Cat. 1991, 70, 363-368; Catal. Lett. 1991, 8, 209-214; J. Organomet. Chem, 1991, 403, 221-227; Nature, 1989, 339, 454-455; J. Catal. 1985, 96, 563-573; J. Mol. Cat. 1987, 39, 243-259.

The metal, e.g., rhodium, catalyst may be attached to a thin film or membrane support, such as cellulose acetate or polyphenylenesulfone, as described in for example J. Mol. Cat. 1990, 63, 213-221.

The metal, e.g., rhodium, catalyst may be attached to an insoluble polymeric support through an organophosphorus-containing ligand, such as a phosphite, incorporated into the polymer. The supported catalyst is not limited by the choice of polymer or

phosphorus-containing species incorporated into it. Descriptions of polymer-supported catalysts may be found in for example: J. Mol. Cat. 1993, 83, 17-35; Chemtech 1983, 46; J. Am. Chem. Soc. 1987, 109, 7122-7127.

In the heterogeneous catalysts described above, the catalyst may remain in its heterogeneous form during the entire hydroformylation and catalyst separation process. In another embodiment of the invention, the catalyst may be supported on a polymer which, by the nature of its molecular weight, is soluble in the reaction medium at elevated temperatures, but precipitates upon cooling, thus facilitating catalyst separation from the reaction mixture. Such "soluble" polymer-supported catalysts are described in for example: Polymer, 1992, 33, 161; J. Org. Chem. 1989, 54, 2726-2730.

More preferably, the reaction is carried out in the slurry phase due to the high boiling points of the products, and to avoid decomposition of the product aldehydes. The catalyst may then be separated from the product mixture, for example, by filtration or decantation. The reaction product fluid may contain a heterogeneous metal-organopolyphosphite ligand complex catalyst, e.g., slurry, or at least a portion of the reaction product fluid may contact a fixed heterogeneous metal-organopolyphosphite ligand complex catalyst during the hydroformylation process. In an embodiment of this invention, the metal-organopolyphosphite ligand complex catalyst may be slurried in the reaction product fluid.

The substituted or unsubstituted olefinic unsaturated starting material reactants that may be employed in the hydroformylation processes of this invention include both optically active (prochiral and chiral) and non-optically active (achiral) olefinic unsaturated compounds containing from 2 to 40, preferably 4 to 20, carbon atoms. Such olefinic unsaturated compounds can be terminally or internally unsaturated and be of straight-chain, branched chain or cyclic structures, as well as olefin mixtures, such as obtained from the

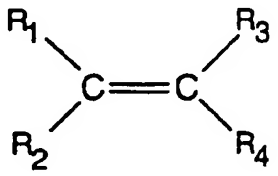
oligomerization of propene, butene, isobutene, etc. (such as so called dimeric, trimeric or tetrameric propylene and the like, as disclosed, for example, in U. S. Patent Nos. 4,518,809 and 4,528,403). Moreover, such olefin compounds may further contain one or more ethylenic unsaturated groups, and of course, mixtures of two or more different olefinic unsaturated compounds may be employed as the starting hydroformylation material if desired. For example, commercial alpha olefins containing four or more carbon atoms may contain minor amounts of corresponding internal olefins and/or their corresponding saturated hydrocarbon and that such commercial olefins need not necessarily be purified from same prior to being hydroformylated. Illustrative mixtures of olefinic starting materials that can be employed in the hydroformylation reactions include, for example, mixed butenes, e.g., Raffinate I and II. Further such olefinic unsaturated compounds and the corresponding aldehyde products derived therefrom may also contain one or more groups or substituents which do not unduly adversely affect the hydroformylation process or the process of this invention such as described, for example, in U. S. Patent Nos. 3,527,809, 4,769,498 and the like.

Most preferably the subject invention is especially useful for the production of non-optically active aldehydes, by hydroformylating achiral alpha-olefins containing from 2 to 30, preferably 4 to 20, carbon atoms, and achiral internal olefins containing from 4 to 20 carbon atoms as well as starting material mixtures of such alpha olefins and internal olefins.

Illustrative alpha and internal olefins include, for example, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 2-butene, 2-methyl propene (isobutylene), 2-methylbutene, 2-pentene, 2-hexene, 3-hexane, 2-heptene, 2-octene, cyclohexene, propylene dimers, propylene trimers, propylene

tetramers, butadiene, piperylene, isoprene, 2-ethyl-1-hexene, styrene, 4-methyl styrene, 4-isopropyl styrene, 4-tert-butyl styrene, alpha-methyl styrene, 4-tert-butyl-alpha-methyl styrene, 1,3-diisopropenylbenzene, 3-phenyl-1-propene, 1,4-hexadiene, 1,7-octadiene, 3-cyclohexyl-1-butene, and the like, as well as, 1,3-dienes, butadiene, alkyl alkenoates, e.g., methyl pentenoate, alkenyl alkanoates, alkenyl alkyl ethers, alkenols, e.g., pentenols, alkenals, e.g., pentenals, and the like, such as allyl alcohol, allyl butyrate, hex-1-en-4-ol, oct-1-en-4-ol, vinyl acetate, allyl acetate, 3-butenyl acetate, vinyl propionate, allyl propionate, methyl methacrylate, vinyl ethyl ether, vinyl methyl ether, allyl ethyl ether, n-propyl-7-octenoate, 3-butenenitrile, 5-hexenamide, eugenol, iso-eugenol, safrole, iso-safrole, anethol, 4-allylanisole, indene, limonene, beta-pinene, dicyclopentadiene, cyclooctadiene, camphene, linalool, and the like.

Prochiral and chiral olefins useful in the asymmetric hydroformylation that can be employed to produce enantiomeric aldehyde mixtures that may be encompassed by in this invention include those represented by the formula:



(VIII)

wherein R_1, R_2, R_3 and R_4 are the same or different (provided R_1 is different from R_2 or R_3 is different from R_4) and are selected from hydrogen; alkyl; substituted alkyl, said substitution being selected from dialkylamino such as benzylamino and dibenzylamino, alkoxy such as methoxy and ethoxy, acyloxy such as acetoxy, halo, nitro, nitrile, thio, carbonyl, carboxamide, carboxaldehyde, carboxyl, carboxylic ester; aryl including phenyl; substituted aryl including

phenyl, said substitution being selected from alkyl, amino including alkylamino and dialkylamino such as benzylamino and dibenzylamino, hydroxy, alkoxy such as methoxy and ethoxy, acyloxy such as acetoxy, halo, nitrile, nitro, carboxyl, carboxaldehyde, carboxylic ester, carbonyl, and thio; acyloxy such as acetoxy; alkoxy such as methoxy and ethoxy; amino including alkylamino and dialkylamino such as benzylamino and dibenzylamino; acylamino and diacylamino such as acetylbenzylamino and diacetylamino; nitro; carbonyl; nitrile; carboxyl; carboxamide; carboxaldehyde; carboxylic ester; and alkylmercapto such as methylmercapto. It is understood that the prochiral and chiral olefins of this definition also include molecules of the above general formula where the R groups are connected to form ring compounds, e.g., 3-methyl-1-cyclohexene, and the like.

Illustrative optically active or prochiral olefinic compounds useful in asymmetric hydroformylation include, for example, p-isobutylstyrene, 2-vinyl-6-methoxy-2-naphthylene, 3-ethenylphenyl phenyl ketone, 4-ethenylphenyl-2-thienylketone, 4-ethenyl-2-fluorobiphenyl, 4-(1,3-dihydro-1-oxo-2H-isoindol-2-yl)styrene, 2-ethenyl-5-benzoylthiophene, 3-ethenylphenyl phenyl ether, propenylbenzene, isobutyl-4-propenylbenzene, phenyl vinyl ether and the like. Other olefinic compounds include substituted aryl ethylenes as described, for example, in U.S. Patent Nos. 4,329,507, 5,360,938 and 5,491,266, the disclosures of which are incorporated herein by reference.

Illustrative of suitable substituted and unsubstituted olefinic starting materials include those permissible substituted and unsubstituted olefinic compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, 1996, the pertinent portions of which are incorporated herein by reference.

The reaction conditions of the hydroformylation processes encompassed by this invention may include any suitable type hydroformylation conditions heretofore employed for producing

optically active and/or non-optically active aldehydes. For instance, the total gas pressure of hydrogen, carbon monoxide and olefin starting compound of the hydroformylation process may range from about 1 to about 10,000 psia. In general, however, it is preferred that the process be operated at a total gas pressure of hydrogen, carbon monoxide and olefin starting compound of less than about 2000 psia and more preferably less than about 500 psia. The minimum total pressure is limited predominately by the amount of reactants necessary to obtain a desired rate of reaction. More specifically the carbon monoxide partial pressure of the hydroformylation process of this invention is preferable from about 1 to about 1000 psia, and more preferably from about 3 to about 800 psia, while the hydrogen partial pressure is preferably about 5 to about 500 psia and more preferably from about 10 to about 300 psia. In general H_2:CO molar ratio of gaseous hydrogen to carbon monoxide may range from about 1:10 to 100:1 or higher, the more preferred hydrogen to carbon monoxide molar ratio being from about 1:10 to about 10:1. Further, the hydroformylation process may be conducted at a reaction temperature from about –25°C to about 200°C. In general hydroformylation reaction temperatures of about 50°C to about 120°C are preferred for all types of olefinic starting materials. Of course it is to be understood that when non-optically active aldehyde products are desired, achiral type olefin starting materials and organopolyphosphite ligands are employed and when optically active aldehyde products are desired prochiral or chiral type olefin starting materials and organopolyphosphite ligands are employed. Of course, it is to be also understood that the hydroformylation reaction conditions employed will be governed by the type of aldehyde product desired.

The hydroformylation processes encompassed by this invention are also conducted in the presence of an organic solvent for the metal-organopolyphosphite ligand complex catalyst and free organopolyphosphite ligand. The solvent may also contain dissolved

water up to the saturation limit. Depending on the particular catalyst and reactants employed, suitable organic solvents include, for example, alcohols, alkanes, alkenes, alkynes, ethers, aldehydes, higher boiling aldehyde condensation byproducts, ketones, esters, amides, tertiary amines, aromatics and the like. Any suitable solvent which does not unduly adversely interfere with the intended hydroformylation reaction can be employed and such solvents may include those disclosed heretofore commonly employed in known metal catalyzed hydroformylation reactions. Mixtures of one or more different solvents may be employed if desired. In general, with regard to the production of achiral (non-optically active) aldehydes, it is preferred to employ aldehyde compounds corresponding to the aldehyde products desired to be produced and/or higher boiling aldehyde liquid condensation byproducts as the main organic solvents as is common in the art. Such aldehyde condensation byproducts can also be preformed if desired and used accordingly. Illustrative preferred solvents employable in the production of aldehydes include ketones (e.g. acetone and methylethyl ketone), esters (e.g. ethyl acetate), hydrocarbons (e.g. toluene), nitrohydrocarbons (e.g. nitrobenzene), ethers (e.g. tetrahydrofuran (THF) and glyme), 1,4-butanediols and sulfolane. Suitable solvents are disclosed in U.S. Patent No. 5,312,996. The amount of solvent employed is not critical to the subject invention and need only be that amount sufficient to solubilize the catalyst and free ligand of the hydroformylation reaction mixture to be treated. In general, the amount of solvent may range from about 5 percent by weight up to about 99 percent by weight or more based on the total weight of the hydroformylation reaction mixture starting material.

Accordingly illustrative non-optically active aldehyde products include e.g., propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, 2-methyl 1-butyraldehyde, hexanal, hydroxyhexanal, 2-methyl valeraldehyde, heptanal, 2-methyl 1-hexanal, octanal, 2-methyl 1-heptanal, nonanal, 2-methyl-1-octanal,

2-ethyl 1-heptanal, 3-propyl 1-hexanal, decanal, adipaldehyde, 2-methylglutaraldehyde, 2-methyladipaldehyde, 3-methyladipaldehyde, 3-hydroxypropionaldehyde, 6-hydroxyhexanal, alkenals, e.g., 2-, 3- and 4-pentenal, alkyl 5-formylvalerate, 2-methyl-1-nonanal, undecanal, 2-methyl 1-decanal, dodecanal, 2-methyl 1-undecanal, tridecanal, 2-methyl 1-tridecanal, 2-ethyl, 1-dodecanal, 3-propyl-1-undecanal, pentadecanal, 2-methyl-1-tetradecanal, hexadecanal, 2-methyl-1-pentadecanal, heptadecanal, 2-methyl-1-hexadecanal, octadecanal, 2-methyl-1-heptadecanal, nonodecanal, 2-methyl-1-octadecanal, 2-ethyl 1-heptadecanal, 3-propyl-1-hexadecanal, eicosanal, 2-methyl-1-nonadecanal, heneicosanal, 2-methyl-1-eicosanal, tricosanal, 2-methyl-1-docosanal, tetracosanal, 2-methyl-1-tricosanal, pentacosanal, 2-methyl-1-tetracosanal, 2-ethyl 1-tricosanal, 3-propyl-1-docosanal, heptacosanal, 2-methyl-1-octacosanal, nonacosanal, 2-methyl-1-octacosanal, hentriacontanal, 2-methyl-1-triacontanal, and the like.

Illustrative optically active aldehyde products include (enantiomeric) aldehyde compounds prepared by the asymmetric hydroformylation process of this invention such as, e.g. S-2-(p-isobutylphenyl)-propionaldehyde, S-2-(6-methoxy-2-naphthyl)propionaldehyde, S-2-(3-benzoylphenyl)-propionaldehyde, S-2-(p-thienoylphenyl)propionaldehyde, S-2-(3-fluoro-4-phenyl)phenylpropionaldehyde, S-2-[4-(1,3-dihydro-1-oxo-2H-isoindol-2-yl)phenyl]propionaldehyde, S-2-(2-methylacetaldehyde)-5-benzoylthiophene and the like.

Illustrative of suitable substituted and unsubstituted aldehyde products include those permissible substituted and unsubstituted aldehyde compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, 1996, the pertinent portions of which are incorporated herein by reference.

As indicated above, it is generally preferred to carry out the hydroformylation processes of this invention in a continuous manner. In general, continuous hydroformylation processes are well

known in the art and may involve: (a) hydroformylating the olefinic starting material(s) with carbon monoxide and hydrogen in a liquid homogeneous reaction mixture comprising a solvent, the metal-organopolyphosphite ligand complex catalyst, and free organopolyphosphite ligand; (b) maintaining reaction temperature and pressure conditions favorable to the hydroformylation of the olefinic starting material(s); (c) supplying make-up quantities of the olefinic starting material(s), carbon monoxide and hydrogen to the reaction medium as those reactants are used up; and (d) recovering the desired aldehyde hydroformylation product(s) in any manner desired. The continuous process can be carried out in a single pass mode, i.e., wherein a vaporous mixture comprising unreacted olefinic starting material(s) and vaporized aldehyde product is removed from the liquid reaction mixture from whence the aldehyde product is recovered and make-up olefinic starting material(s), carbon monoxide and hydrogen are supplied to the liquid reaction medium for the next single pass without recycling the unreacted olefinic starting material(s). Such types of recycle procedure are well known in the art and may involve the liquid recycling of the metal-organopolyphosphite complex catalyst fluid separated from the desired aldehyde reaction product(s), such as disclosed, for example, in U.S. Patent 4,148,830 or a gas recycle procedure such as disclosed, for example, in U.S. Patent 4,247,486, as well as a combination of both a liquid and gas recycle procedure if desired. The disclosures of said U.S. Patents 4,148,830 and 4,247,486 are incorporated herein by reference thereto. The most preferred hydroformylation process of this invention comprises a continuous liquid catalyst recycle process. Suitable liquid catalyst recycle procedures are disclosed, for example, in U. S. Patent Nos. 4,668,651; 4,774,361; 5,102,505 and 5,110,990.

In an embodiment of this invention, the aldehyde product mixtures may be separated from the other components of the crude reaction mixtures in which the aldehyde mixtures are produced by any

suitable method. Suitable separation methods include, for example, solvent extraction, crystallization, distillation, vaporization, wiped film evaporation, falling film evaporation, phase separation, filtration and the like. It may be desired to remove the aldehyde products from the crude reaction mixture as they are formed through the use of trapping agents as described in published Patent Cooperation Treaty Patent Application WO 88/08835. A preferred method for separating the aldehyde mixtures from the other components of the crude reaction mixtures is by membrane separation. Such membrane separation can be achieved as set out in U.S. Patent No. 5,430,194 and copending U.S. Patent Application Serial No. 08/430,790, filed May 5, 1995, referred to above.

As indicated above, at the conclusion of (or during) the process of this invention, the desired aldehydes may be recovered from the reaction mixtures used in the process of this invention. For example, the recovery techniques disclosed in U.S. Patents 4,148,830 and 4,247,486 can be used. For instance, in a continuous liquid catalyst recycle process the portion of the liquid reaction mixture (containing aldehyde product, catalyst, etc.), i.e., reaction product fluid, removed from the reaction zone can be passed to a separation zone, e.g., vaporizer/separator, wherein the desired aldehyde product can be separated via distillation, in one or more stages, under normal, reduced or elevated pressure, from the liquid reaction fluid, condensed and collected in a product receiver, and further purified if desired. The remaining non-volatilized catalyst containing liquid reaction mixture may then be recycled back to the reactor as may if desired any other volatile materials, e.g., unreacted olefin, together with any hydrogen and carbon monoxide dissolved in the liquid reaction after separation thereof from the condensed aldehyde product, e.g., by distillation in any conventional manner. In general, it is preferred to separate the desired aldehydes from the catalyst-containing reaction mixture under reduced pressure and at low temperatures so as to avoid possible

degradation of the organopolyphosphite ligand and reaction products. When an alpha-mono-olefin reactant is also employed, the aldehyde derivative thereof can also be separated by the above methods.

More particularly, distillation and separation of the desired aldehyde product from the metal-organopolyphosphite complex catalyst containing reaction product fluid may take place at any suitable temperature desired. In general, it is recommended that such distillation take place at relatively low temperatures, such as below 150°C, and more preferably at a temperature in the range of from about 50°C to about 140°C. It is also generally recommended that such aldehyde distillation take place under reduced pressure, e.g., a total gas pressure that is substantially lower than the total gas pressure employed during hydroformylation when low boiling aldehydes (e.g., C_4 to C_6) are involved or under vacuum when high boiling aldehydes (e.g. C_7 or greater) are involved. For instance, a common practice is to subject the liquid reaction product medium removed from the hydroformylation reactor to a pressure reduction so as to volatilize a substantial portion of the unreacted gases dissolved in the liquid medium which now contains a much lower synthesis gas concentration than was present in the hydroformylation reaction medium to the distillation zone, e.g. vaporizer/separator, wherein the desired aldehyde product is distilled. In general, distillation pressures ranging from vacuum pressures on up to total gas pressure of about 50 psig should be sufficient for most purposes.

As stated above, the subject invention resides in the discovery that metal, e.g., rhodium, catalyst deactivation as discussed herein can be minimized or prevented by carrying out such separation of the desired aldehyde product from such metal-organopolyphosphite ligand catalyst containing product solutions in the added presence of one or more free heterocyclic nitrogen compounds having a five or six membered heterocyclic ring consisting of 2 to 5 carbon atoms and from 2 to 3 nitrogen atoms, at least one of said nitrogen atoms containing a

double bond. Such free heterocyclic nitrogen compounds may be selected from diazole, triazole, diazine, and triazine compounds. The term "free" as it applies to said heterocyclic nitrogen compounds is employed herein to exclude any acid salts of such heterocyclic nitrogen compounds employable in this invention, i.e., salt compounds formed by the reaction of any acid e.g., H_3PO_4, with such free heterocyclic nitrogen compounds.

At carbon monoxide partial pressures sufficiently low, e.g., less than about 10 psi, to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, the one or more free heterocyclic nitrogen compounds (i) have a coordination strength with respect to the metal of said metal-organopolyphosphite ligand complex catalyst sufficient to effect at least some coordination with the metal of said metal-organopolyphosphite ligand complex catalyst, i.e., sufficient to compete with carbon monoxide to effect at least some coordination with the metal of said metal-organopolyphosphite ligand complex catalyst, and (ii) have a coordination strength with respect to the metal of said metal-organopolyphosphite ligand complex catalyst less than the organopolyphosphite ligand of said metal-organopolyphosphite ligand complex catalyst, i.e., sufficient not to compete with coordination of the organopolyphosphite ligand with the metal of said metal-organopolyphosphite ligand complex catalyst.

Without wishing to be bound to any exact theory or mechanistic discourse it is believed that the encountered slow loss in catalytic activity of organopolyphosphite promoted metal hydroformylation catalysts is due at least in part to the harsh conditions such as employed in the separation and recovery of the aldehyde product from its reaction product fluid. For instance it has been found that when an organopolyphosphite promoted rhodium catalyst is placed under harsh conditions such as high temperature and low carbon monoxide partial pressure such as occur in a vaporizer, that the catalyst deactivates at an accelerated pace with time, due most

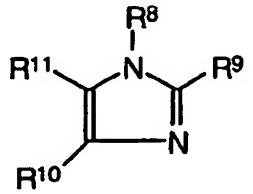
likely to the formation of an inactive or less active rhodium species, which may also be susceptible to precipitation under prolonged exposure to such conditions. Such evidence is also consistent with the view that the active catalyst which under hydroformylation conditions is believed to comprise a complex of rhodium, organopolyphosphite, carbon monoxide and hydrogen, losses at least some of its coordinated carbon monoxide ligand during harsh conditions such as exist during separation, e.g., vaporization, which provides a route for the formation of such catalytically inactive or less active rhodium species as discussed above. The means for preventing or minimizing such catalyst deactivation and/or precipitation comprises carrying out the portion of the hydroformylation process that involves harsh conditions such as the separation, e.g., vaporization, procedure of the hydroformylation process in the presence of one or more free heterocyclic nitrogen compounds as disclosed herein.

By way of further explanation it is believed the free heterocyclic nitrogen compound serves as a replacement ligand for the lost carbon monoxide ligand thereby forming a neutral intermediate metal, e.g., rhodium, species comprising a complex of metal, organopolyphosphite, the heterocyclic nitrogen compound and hydrogen during such separation under harsh conditions such as exist in a vaporizer, thereby preventing or minimizing the formation of any such above mentioned catalytic inactive or less active rhodium species. It is further theorized that the maintenance of catalytic activity, or the minimization of its deactivation, throughout the course of such continuous liquid recycle hydroformylation is due to regeneration of the active catalyst from said neutral intermediate rhodium species in the reactor (i.e. hydroformylation reaction zone) of the particular hydroformylation process involved. It is believed that under the higher syn gas pressure hydroformylation conditions in the reactor, the active catalyst complex comprising metal, e.g., rhodium, organopolyphosphite, carbon monoxide and hydrogen is regenerated as

a result of some of the carbon monoxide in the reactant syn gas replacing the heterocyclic nitrogen ligand of the recycled neutral intermediate rhodium species. That is to say, carbon monoxide having a stronger ligand affinity for rhodium, replaces the more weakly bonded heterocyclic nitrogen ligand of the recycled neutral intermediate rhodium species that was formed during vaporization separation as mentioned above, thereby reforming the active catalyst in the hydroformylation reaction zone. In any event, regardless of the specific mechanism involved regarding the formation of an intermediate rhodium species and/or the regeneration of active catalyst, it should be sufficient to note, that the use of such free heterocyclic nitrogen compounds in accordance with this invention is considered to be excellent means for preventing or minimizing catalytic activity loss of organopolyphosphite promoted metal, e.g., rhodium, hydroformylation catalysts due to harsh conditions such as encountered in vaporization separation of the aldehyde product from its reaction production fluid.

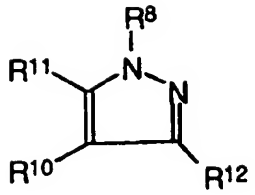
Illustrative diazole compounds include the following:

(a) imidazoles represented by the formula:



(IX)

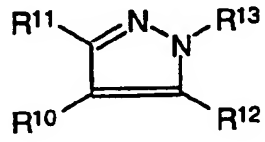
(b) pyrazoles represented by the formula:



(X)

and

(c) indazoles represented by the formula:



(XI)

wherein in Formulas (IX), (X) and (XI) above, R^8, R^9, R^{10}, R^{11}, R^{12} and R^{13} are identical or different and each represents a hydrogen atom or a monovalent substituent, with the proviso that $R^8$and R^9 should not both be monovalent hydrocarbon radicals at the same time. The adjacent substituents R^8 and R^{11}, or R^8 and R^9, or R^{10} and R^{11}, or R^{10} and R^{12}, or R^{12} and R^{13} may optionally be taken together to form a substituted or unsubstituted divalent radical which together with the two atoms of the formula to which said adjacent substituents are bonded form a cyclic ring.

The monovalent R^8 to R^{13} substituents in Formulas (IX) , (X) and (XI) can be any substituent that does not unduly adversely affect the purpose and process of this invention. Examples of such monovalent substituents include hydroxy, cyano, nitro, trifluoromethyl and substituted or unsubstituted radicals containing from 1 to 30 carbon atoms selected from the group consisting, acyl, acyloxy carbonyloxy, oxycarbonyl, silyl, alkoxy, aryloxy, cycloalkoxy, alkyl, aryl, alkaryl, aralkyl, and alicyclic radicals.

More specifically illustrative monovalent substituents containing from 1 to 30 carbon atoms include e.g., primary, secondary and tertiary alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, neo-pentyl, n-hexyl, amyl, sec-amyl, t-amyl, iso-octyl, decyl, octadecyl, and the like; aryl radicals such as phenyl, naphthyl and the like; aralkyl radicals such as benzyl, phenylethyl, triphenylmethyl, and the like; alkaryl radicals such as tolyl, xylyl, and the like; alicyclic radicals such as cyclopentyl, cyclohexyl, 1-methylcyclohexyl, cyclooctyl, cyclohexylethyl, and the like; alkoxy radicals such as methoxy, ethoxy, propoxy, t-butoxy $-OCH_2CH_2OCH_3$, $-O(CH_2CH_2)_2OCH_3$, $-O(CH_2CH_2)_3OCH_3$, and the like; aryloxy radicals such as phenoxy and the like; as well as silyl radicals such as $-Si(CH_3)_3$, $-Si(OCH_3)_3$, $-Si(C_3H_7)_3$, and the like; acyl radicals such as $-C(O)CH_3$, $-C(O)C_2H_5$, $-C(O)C_6H_5$, and the like; carbonyloxy radicals such as $-C(O)OCH_3$ and the like; oxycarbonyl radicals such as $-O(CO)C_6H_5$, and the like.

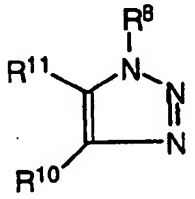
Of course if desired such monovalent substituents may in turn be substituted with any substituent which does not unduly adversely affect the purpose and process of this invention such as, for example, those hydrocarbon and non-hydrocarbon substituents outlined herein for R^8, R^9, R^{10}, R^{11}, R^{12} and R^{13}. It is to be further understood that Formulas (IX) through (XI) are also intended to encompass compounds having two or more such diazole formulas, e.g., wherein two diazole formulas are directly bonded together as a result of any one of the R^8 to R^{13} substituents optionally representing a direct bond or as a result of any one of the R^8 to R^{13} substituents being optionally substituted with a second diazole formula.

Moreover, said adjacent substituents, R^8 and R^{11}, or R^8 and R^9, or R^{10} and R^{11}, or R^{10} and R^{12}, or R^{12} and R^{13}, may be taken together to form a substituted or unsubstituted divalent bridging group having from 3 to 5, preferably 4, carbon atoms, which along with

the two atoms shown in the formula to which they are bonded, form a 5 to 7 membered cyclic ring. Such divalent bridging groups preferably consist of only carbon atoms, but may contain from 1 to 2 nitrogen atoms in addition to said carbon atoms. Examples of substituents that may be on the substituted divalent bridging groups are the same hydrocarbon and non-hydrocarbon substituents as those defined herein for R^8, R^9, R^{10}, R^{11}, R^{12} and R^{13}. Preferred diazoles are the imidazoles of Formula (IX) above, especially benzimidazoles.

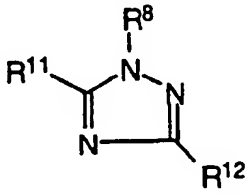
Illustrative triazole compounds include the following:

(a) 1,2,3-triazoles represented by the formula:



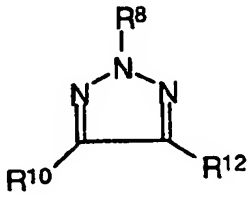
(XII)

(b) 1,2,4-triazoles represented by the formula:



(XIII)

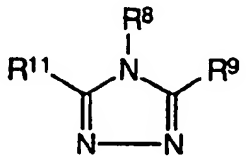
(c) 2,1,3-triazoles represented by the formula:



(XIV)

and

(d) 4,1,2-triazoles represented by the formula:



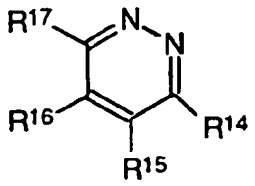
(XV)

wherein in Formulas (XII), (XIII), (XIV), and (XV) above, R^8, R^9, R^{10}, R^{11} and R^{12} are identical or different and each represents a hydrogen atom or a monovalent substituent, and adjacent substituents R^8 and R^9, or R^8 and R^{11}, or R^{10} and R^{11}, or R^{10}, and R^{12}, may optionally be taken together to form a substituted or unsubstituted divalent radical which together with the two atoms of the formula to which said adjacent substituents are bonded form a cyclic ring. More specifically said monovalent substituents of R^8, R^9, R^{10}, R^{11} and R^{12} and the adjacent substituents R^8 and R^9, R^8 and R^{11}, R^{10} and R^{11}, or R^{10} and R^{12}, in Formulas (XII) to (XV) above, may be the same as the monovalent substituents and divalent radicals defined for Formulas (IX) to (XI) above. It is to be further understood that Formulas (XII) through (XV) are also intended to encompass compounds having two or more such triazole formulas, e.g., wherein two triazole formulas are directly bonded together as a result of any one of the R^8, R^9, R^{10}, R^{11} and R^{12} substituents optionally representing a direct bond or as a result of any one of the R^8, R^9, R^{10}, R^{11} and R^{12} substituents being optionally substituted with a second triazole formula. Preferred triazoles are the 1,2,3-triazoles of Formula (XII) above, especially benzotriazole. Other illustrative triazoles include 5-methyl-1H-benzotriazole, 5,6-dimethyl-1-H-benzotriazole, 1-hydroxybenzotriazole, 2-(2H-benzotriazole-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol, 5-nitrobenzotriazole, bis(1-benzotriazolyl)oxalate, 1-benzotriazolyl 9-fluorenylmethyl carbonate, 1-cyanobenzotriazole, 2-(2H-benzotriazol-2-

yl)-hydroquinone, 2-(2-hydroxy-5-methylphenyl)-benzotriazole, 5-hexylbenzotriazole, 5-decylbenzotriazole, 1-ethylbenzotriazole, 1-pentylbenzotriazole, 1-benzylbenzotriazole, 1-dodecylbenzotriazole, and the like.

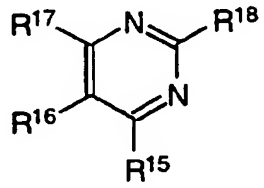
Illustrative diazine compounds include the following:

(a) 1,2-diazines represented by the formula:



(XVI)

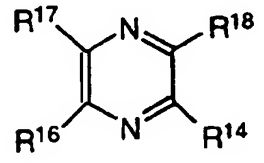
(b) 1,3-diazines represented by the formula:



(XVII)

and

(c) 1,4-diazines represented by the formula:



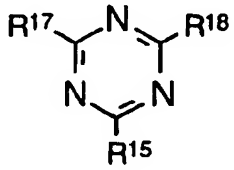
(XVIII)

wherein in Formulas (XVI), (XVII) and (XVIII) above, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} are identical or different and each represents a hydrogen atom or a monovalent substituent, and adjacent substituents R^{14} and R^{15}, or R^{15} and R^{16}, or R^{16} and R^{17}, or R^{14} and R^{18} may optionally

be taken together to form a substituted or unsubstituted divalent radical which together with the two atoms of the formula to which said adjacent substituents are bonded form a cyclic ring. More specifically, said monovalent substituents R^{14}, R^{15}, R^{16}, R^{17} and R^{18}, and the adjacent substituents R^{14} and R^{15}, or R^{15} and R^{16}, or R^{16} and R^{17}, or R^{14} and R^{18}, in Formulas (XVI) to (XVIII) above, may be the same as the monovalent substituents and divalent radicals defined for Formulas (IX) to (XI) above. It is to be further understood that Formulas (XVI) through (XVIII) are also intended to encompass compounds having two or more such diazine formulas, e.g., wherein two diazine formulas are directly bonded together as a result of any one of the R^{14} to R^{18} substituents optionally representing a direct bond or as a result of any one of the R^{14} to R^{18} substituents being optionally substituted with a second diazine formula. Illustrative of such diazine compounds are pyridazine, pyrimidine, pyrazine, and the like.

Illustrative triazine compounds include the following:

(a) 1,3,5-triazines represented by the formula:



(XIX)

wherein in Formula (XIX) above, R^{15}, R^{17}, and R^{18} are identical or different and each represents a hydrogen atom or a monovalent substituent. More specifically, said monovalent substituents R^{15}, R^{17}, and R^{18} in Formula (XIX) above, may be the same as the monovalent substituents defined for Formulas (IX) to (XI) above. It is to be further understood that Formulas (XIX) is also intended to encompass compounds having two or more such triazine formulas, e.g., wherein two triazine formulas are directly bonded together as a result of any

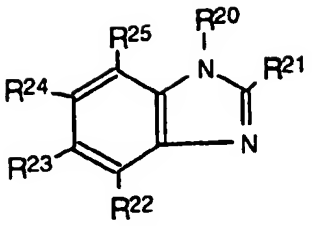
one of the R^{15}, R^{17}, and R^{18} substituents optionally representing a direct bond or as a result of any one of the R^{15}, R^{17}, and R^{18} substituents being optionally substituted with a second triazine formula. Illustrative of such triazines compounds are 1,3,5-triazine, and the like.

Of course any of the R^8 to R^{18} radicals of such free heterocyclic nitrogen compounds of Formulas (IX) to (XIX) above may be substituted if desired, with any suitable substituent containing from 1 to 30 carbon atoms that does not unduly adversely affect the desired result of the process or this invention. Substituents that may be on said radicals in addition of course to corresponding hydrocarbon radicals such as alkyl, aryl, aralkyl, alkaryl and cyclohexyl substituents, may include for example amino radicals such as -$N(R^{19})_2$; phosphine radicals such as -aryl-$P(R^{19})_2$; acyl radicals such as -$C(O)R^{19}$ acyloxy radicals such as -$OC(O)R^{19}$; amido radicals such as -$CON(R^{19})_2$ and -$N(R^{19})COR^{19}$; sulfonyl radicals such as -SO_2R^{19}, alkoxy radicals such as -OR^{19}, sulfinyl radicals such as -SOR^{19}, sulfenyl radicals such as -SR^{19}, ionic radicals selected from the group consisting of: -SO_3M, -PO_3M, -$N(R^6)_3X^1$ and -CO_2M as defined herein above for ionic phosphites, wherein M, X^1 and R^6 are as defined above, as well as, halogen, nitro, cyano, trifluoromethyl, hydroxy radicals, and the like, wherein each R^{19} radical individually represents the same or different monovalent hydrocarbon radical having from 1 to 18 carbon atoms (e.g., alkyl, aryl, aralkyl, alkaryl and cyclohexyl radicals), with the proviso that in amino substituents such as -$N(R^{19})_2$ each R^{19} taken together can also represent a divalent bridging group that forms a heterocyclic radical with the nitrogen atom. Of course it is to be understood that any of the substituted or unsubstituted substituent radicals that make up a particular given free heterocyclic nitrogen compound may be the same or different.

The more preferred free heterocyclic nitrogen compounds employable in this invention are the imidazoles of Formula (IX) above, especially benzimidazoles.

Illustrative specific examples include imidazole and substituted imidazoles, such as 1-methylimidazole, 1-ethylimidazole, 1-n-propylimidazole, 1-isopropylimidazole, 1-butylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-n-propylimidazole, 2-isopropylimidazole, 2-n-butylimidazole, 2-n-hexylimidazole, 2-n-heptylimidazole, 2-n-octylimidazole, 2-n-nonylimidazole, 2-n-decyl-imidazole, 2-n-undecylimidazole, 2-n-dodecylimidazole, 2-n-tridecylimidazole, 2-n-tetradecylimidazole, 2-n-pentadecylimidazole, 2-n-hexadecylimidazole, 2-n-heptadecylimidazole, 2-(2-ethylpentyl)imidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 1-benzyl-2-methylimidazole, 2,4,5-triphenylimidazole, 2-(2-propylhexyl)imidazole, 4-methylimidazole, 4-ethylimidazole, 3-n-propylimidazole, 4-isopropylimidazole, 4-butylimidazole, 4,5-dimethylimidazole, 4,5-diethylimidazole, 1-methyl-2-ethylimidazole, 1-methyl-4-ethylimidazole, 2-ethyl-4-methylimidazole, 1-benzyl-2-methylimidazole, 1-phenylimidazole, 2-phenylimidazole, 4-phenylimidazole, 2,4,5-triphenylimidazole, 1,2-trimethyleneimidazole, 1,5-trimethyleneimidazole, 4,5-trimethyleneimidazole, and the like, as well as, polar substituted imidazoles, such as e.g., 1-hydroxymethylimidazole, 2-hydroxymethylimidazole, 4-hydroxymethylimidazole, 1-(2-hydroxyethyl)imidazole, 2(2-hydroxyethyl)imidazole, 4-2(hydroxyethyl)imidazole, 1-carboxymethylimidazole, 2-carboxymethylimidazole, 4-carboxymethylimidazole, 1(2-carboxyethyl)imidazole, 4-(2-carboxyethyl)imidazole, 4-(2-carboxyethyl)imidazole, 4-(2-carboxy-2-hydroxyethyl)imidazole, and the like.

. The even more preferred benzimidazoles employable in this invention are those represented by the formula:



(XX)

wherein in Formula (XX) above R^{20}, R^{21}, R^{22}, R^{23}, R^{24} and R^{25} are identical or different and each represent a hydrogen atom or a monovalent substituent, provided R^{20} and R^{21} are not both a monovalent hydrocarbon radical at the same time. More specifically said monovalent substituents of R^{20}, R^{21}, R^{22}, R^{23}, R^{24} and R^{25} may be the same as those monovalent substituents defined for Formulas (IX) to (XI) above. Of course it is to be further understood that Formula (XX) is also intended to encompass compounds having two or more such benzimidazole formulas, e.g., wherein two benzimidazole formulas are directly bonded together as a result of any one of the R^{20} to R^{25} substituents, e.g., R^{21}, optionally representing a direct bond or as a result of any one of the R^{20} to R^{25} substituents, e.g., R^{21}, being optionally substituted with a second benzimidazole formula., e.g., di-, bi-, or bis-benzimidazoles.

Illustrative specific examples of such benzimidazoles include benzimidazole and substituted benzimidazoles, such as 1-methylbenzimidazole, 1-ethylbenzimidazole, 1-n-propylbenzimidazole, 1-isopropylbenzimidazole, 1-butylbenzimidazole, 1-benzylbenzimidazole, 2-benzylbenzimidazole, 2-methylbenzimidazole, 2-ethylbenzimidazole, 2-n-propylbenzimidazole, 2-isopropylbenzimidazole, 2-n-butylbenzimidazole, 2-n-hexylbenzimidazole, 2-n-heptylbenzimidazole, 2-n-octylbenzimidazole, 2-n-nonylbenzimidazole, 2-n-decylbenzimidazole, 2-n-undecylbenzimidazole, 2-n-dodecylbenzimidazole,

2-n-tridecylbenzimidazole, 2-n-tetradecylbenzimidazole,
2-n-pentadecylbenzimidazole, 2-n-hexadecylbenzimidazole,
2-n-heptadecylbenzimidazole, 2-(2-ethylpentyl)benzimidazole,
2-(2-propylhexyl)benzimidazole, 2-phenylbenzimidazole,
2-phenylbenzimidazole, 1-benzylimidazole,
1-, cyclohexylbenzimidazole, 1-octylbenzimidazole,
1-dodecylbenzimidazole, 1-hexyldecylbenzimidazole,
5,6-dimethylbenzimidazole, 1-methyl-5,6-dimethylbenzimidazole,
4-methylbenzimidazole, 4-ethylbenzimidazole,
3-n-propylbenzimidazole, 4-isopropylbenzimidazole,
4-butylbenzimidazole, 4,5-dimethylbenzimidazole,
4,5-diethylbenzimidazole, 1-methyl-2-ethylbenzimidazole,
1-methyl-4-ethylbenzimidazole, 1-phenylbenzimidazole, and
4-phenylbenzimidazole, 5-bromobenzotriazole, 6-bromobenzotriazole,
5- chlorobenzotriazole, 6- chlorobenzotriazole,
5-chloro-1,6-dimethylbenzotriazole
5-chloro-6-methylbenzotriazole, 6-chloro-5-methylbenzotriazole,
5-chloro-6-methyl-1-phenylbenzotriazole,
4,5,6,7-tetrachlorobenzotriazole, 1-(2-iodoethyl)benzotriazole,
5-chloro-6-fluorobenzotriazole,5-trifluoromethylbenzotriazole,
6-trifluoromethylbenzotriazole, and the like, as well as, polar
substituted benzimidazoles, such as 1-acetylbenzimidazole,
1-benzoylbenzimidazole, 1-hydroxymethylbenzimidazole,
2-hydroxymethylbenzimidazole, 4-hydroxymethylbenzimidazole,
1-(2-hydroxyethyl)benzimidazole, 2(2-hydroxyethyl)benzimidazole,
4-2(hydroxyethyl)benzimidazole, 1-carboxymethylbenzimidazole,
2-carboxymethylbenzimidazole, 4-carboxymethylbenzimidazole,
1(2-carboxyethyl)benzimidazole, 4-(2-carboxyethyl)benzimidazole,
4-(2-carboxyethyl)benzimidazole, 4-(2-carboxy-2-
hydroxyethyl)benzimidazole, 1-ethyl-5,6-dimethylbenzimidazole,
1-isopropyl-5,6-benzimidazole, 1-isopropyl-5,6-benzimidazole,

5,6-dimethoxybenzimidazole, 4,5-trimethylenebenzimidazole, naphtho[1,2-d]imidazole, naphtho[2,3-d]imidazole, 1-methyl-4-methoxybenzimidazole, 1-methyl-5-methoxybenzimidazole, 1-methyl-5,6-dimethoxybenzimidazole, and the like. Bi-, di- and bis-benzimidazoles are also included such as 2,2'-ethylenebibenzimidazole, 2,2'-heptamethylenebibenzimidazole, 2,2'-hexamethylenebibenzimidazole, 2,2'(iminodiethylidene)-bibenzimidazole, 2,2'-(methyliminodiethylidene)bibenzimidazole, 2,2'-octamethylenebibenzimidazole, 2,2'pentamethylenebibenzimidazole, 2,2-p-phenylenebibenzimidazole, 2,2'-trimethylenebibenzimidazole, 2,2'-methylene bis(5,6-dimethylbenzimidazole), di-2-benzimidazolylmethane, 5,5',6,6'-tetramethyl-2,2'-bibenzimidazole and 1,2-bis(5,6-dimethyl-2-benzimidazolyl)ethanol hydrochloride, and the like. The most preferred heterocyclic nitrogen compound of all is benzimidazole.

Accordingly the free heterocyclic nitrogen compounds which are employable herein are well known compounds as are methods for their preparation and in many instances are readily available commercially. Moreover it is to be understood that while it may be preferred to employ only one free heterocyclic nitrogen compound at a time in any given hydroformylation process, if desired, mixtures of two or more different free heterocyclic nitrogen compounds may also be employed in any given process. Illustrative of suitable substituted and unsubstituted heterocyclic nitrogen compounds include those permissible substituted and unsubstituted heterocyclic nitrogen compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, 1996, the pertinent portions of which are incorporated herein by reference.

Moreover the amount of such free heterocyclic nitrogen compounds employable in any given process of this invention need only be that minimum amount necessary to furnish the basis for at least some minimization of such catalyst deactivation as might be found to

occur as a result of carrying out an identical metal catalyzed hydroformylation process under essentially the same conditions, in the absence of any free heterocyclic nitrogen compound during harsh conditions such as vaporization separation of the aldehyde product. Amounts of such free heterocyclic nitrogen compounds ranging from about 0.01 up to about 10 weight percent, or higher if desired, based on the total weight of the hydroformylation reaction product fluid to be distilled should be sufficient for most purposes. It is of course to be understood that as the aldehyde product is distilled from the hydroformylation product fluid, the concentration of the non-volatilized components therein, e.g. the catalyst and free heterocyclic nitrogen compound, will increase accordingly. Thus the upper amount of free heterocyclic nitrogen compound is governed primarily by its solubility limit in the non-volatilized liquid rhodium catalyst containing residue obtained after such vaporization separation of the aldehyde product, i.e., distillation removal of as much of the aldehyde product desired. Such amounts of the free heterocyclic nitrogen compound employable herein will also depend in part upon the particular rhodium catalyst employed and the distillation temperature for recovering the aldehyde product, as well as the particular free heterocyclic nitrogen compound itself. In general preferred minor amounts of the free heterocyclic nitrogen compound present during the distillation of the desired aldehyde product from the metal-organopolyphosphite catalyst containing product fluids of this invention may range from about 0.05 to about 5 weight percent based on the total weight of the hydroformylation reaction product fluid to be distilled.

The addition of the free heterocyclic nitrogen compound employable in this invention to the reaction product fluid from which the aldehyde product is to be distilled may be carried out in any suitable manner desired. For instance, the free heterocyclic nitrogen compound may be added to the hydroformylation reaction product fluid that has been removed from the reaction zone and at any time prior to

or during the distillation of the aldehyde product therefrom. However, since the free heterocyclic nitrogen compound chosen to be used should not have any substantial detrimental affect on the hydroformylation reaction per se, the free heterocyclic nitrogen compound may be added directly to the hydroformylation reaction medium in the reaction zone and allowed to remain in solution throughout the entire hydroformylation process. Indeed, it may be desirable to add the free heterocyclic nitrogen compound to the precursor catalyst solution to be employed so that the free heterocyclic nitrogen compound is present right from the start of the hydroformylation process.

Another problem that has been observed when organophosphite ligand promoted metal catalysts are employed in olefin hydroformylation processes that involves degradation of the organophosphite ligand and catalyst deactivation of the metal-organophosphite complex catalyzed hydroformylation processes due to the hydrolytic instability of the organophosphite ligands. A means for preventing or minimizing such catalyst deactivation and/or precipitation involves carrying out the invention described and taught in copending U.S. Patent Application Serial Nos. (D-17245-1) and (D-17646), both filed on an even date herewith, the disclosures of which are incorporated herein by reference, which comprises using an aqueous buffer solution and optionally organic nitrogen compounds as disclosed therein.

For instance, said aqueous buffer solution invention comprises treating at least a portion of a metal-organopolyphosphite ligand complex catalyst containing reaction product fluid derived from said hydroformylation process and which also contains phosphorus acidic compounds formed during said hydroformylation process, with an aqueous buffer solution in order to neutralize and remove at least some amount of the phosphorus acidic compounds from said reaction product fluid, and then returning the treated reaction product fluid to the hydroformylation reaction zone or separation zone. Illustrative

phosphorus acidic compounds include, for example, H_3PO_3, aldehyde acids such as hydroxy alkyl phosphonic acids, H_3PO_4 and the like. Said treatment of the metal-organopolyphosphite ligand complex catalyst containing reaction product fluid with the aqueous buffer solution may be conducted in any suitable manner or fashion desired that does not unduly adversely affect the basic hydroformylation process from which said reaction product fluid was derived.

Thus, for example, the aqueous buffer solution may be used to treat all or part of a reaction medium of a continuous liquid catalyst recycle hydroformylation process that has been removed from the reaction zone at any time prior to or after separation of the aldehyde product therefrom. More preferably said aqueous buffer treatment involves treating all or part of the reaction product fluid obtained after distillation of as much of the aldehyde product desired, e.g. prior to or during the recycling of said reaction product fluid to the reaction zone. For instance, a preferred mode would be to continuously pass all or part (e.g. a slip stream) of the recycled reaction product fluid that is being recycled to the reaction zone through a liquid extractor containing the aqueous buffer solution just before said catalyst containing residue is to re-enter the reaction zone.

Thus it is to be understood that the metal-organopolyphosphite ligand complex catalyst containing reaction product fluid to be treated with the aqueous buffer solution may contain in addition to the catalyst complex and its organic solvent, aldehyde product, free phosphite ligand, unreacted olefin, and any other ingredient or additive consistent with the reaction medium of the hydroformylation process from which said reaction product fluids are derived.

Typically maximum aqueous buffer solution concentrations are only governed by practical considerations. As noted, treatment conditions such as temperature, pressure and contact time may also vary greatly and any suitable combination of such

conditions may be employed herein. In general liquid temperatures ranging from about 20°C to about 80°C and preferably from about 25°C to about 60°C should be suitable for most instances, although lower or higher temperatures could be employed if desired. Normally the treatment is carried out under pressures ranging from ambient to reaction pressures and the contact time may vary from a matter of seconds or minutes to a few hours or more.

Moreover, success in removing phosphorus acidic compounds from the reaction product fluid may be determined by measuring the rate degradation (consumption) of the organopolyphosphite ligand present in the hydroformylation reaction medium. In addition as the neutralization and extraction of phosphorus acidic compounds into the aqueous buffer solution proceeds, the pH of the buffer solution will decrease and become more and more acidic. When the buffer solution reaches an unacceptable acidity level it may simply be replaced with a new buffer solution.

The aqueous buffer solutions employable in this invention may comprise any suitable buffer mixture containing salts of oxyacids, the nature and proportions of which in the mixture, are such that the pH of their aqueous solutions may range from 3 to 9, preferably from 4 to 8 and more preferably from 4.5 to 7.5. In this context suitable buffer systems may include mixtures of anions selected from the group consisting of phosphate, carbonate, citrate and borate compounds and cations selected from the group consisting of ammonium and alkali metals, e.g. sodium, potassium and the like. Such buffer systems and/or methods for their preparation are well known in the art.

Preferred buffer systems are phosphate buffers and citrate buffers, e.g. monobasic phosphate/dibasic phosphates of an alkali metal and citrates of an alkali metal. More preferred are buffer systems consisting of mixtures of the monobasic phosphate and the dibasic phosphate of sodium or potassium.

Optionally, an organic nitrogen compound may be added to the hydroformylation reaction product fluid to scavenge the acidic hydrolysis byproducts formed upon hydrolysis of the organopolyphosphite ligand, as taught, for example, in U.S. Patent No. 4,567,306, copending U.S. Patent Application Serial Nos. (D-17245-1) and (D-17646), referred to herein. Such organic nitrogen compounds may be used to react with and to neutralize the acidic compounds by forming conversion product salts therewith, thereby preventing the rhodium from complexing with the acidic hydrolysis byproducts and thus helping to protect the activity of the metal, e.g., rhodium, catalyst while it is present in the reaction zone under hydroformylation conditions. The choice of the organic nitrogen compound for this function is, in part, dictated by the desirability of using a basic material that is soluble in the reaction medium and does not tend to catalyze the formation of aldols and other condensation products at a significant rate or to unduly react with the product aldehyde.

Such organic nitrogen compounds may contain from 2 to 30 carbon atoms, and preferably from 2 to 24 carbon atoms. Primary amines should be excluded from use as said organic nitrogen compounds. Preferred organic nitrogen compounds should have a distribution coefficient that favors solubility in the organic phase. In general more preferred organic nitrogen compounds useful for scavenging the phosphorus acidic compounds present in the hydroformylation reaction product fluid of this invention include those having a pKa value within $\pm$ 3 of the pH of the aqueous buffer solution employed. Most preferably the pKa value of the organic nitrogen compound will be essentially about the same as the pH of the aqueous buffer solution employed. Of course it is to be understood that while it may be preferred to employ only one such organic nitrogen compound at a time in any given hydroformylation process, if desired, mixtures of two or more different organic nitrogen compounds may also be employed in any given processes.

Illustrative organic nitrogen compounds include e.g., trialkylamines, such as triethylamine, tri-n-propylamine, tri-n-butylamine, tri-iso-butylamine, tri-iso-propylamine, tri-n-hexylamine, tri-n-octylamine, dimethyl-iso-propylamine, dimethyl-hexadecylamine, methyl-di-n-octylamine, and the like, as well as substituted derivatives thereof containing one or more noninterfering substituents such as hydroxy groups, for example triethanolamine, N-methyl-di-ethanolamine, tris-(3-hydroxypropyl)-amine, and the like. Heterocyclic amines can also be used such as pyridine, picolines, lutidines, collidines, N-methylpiperidine, N-methylmorpholine, N-2'-hydroxyethylmorpholine, quinoline, iso-quinoline, quinoxaline, acridien, quinuclidine, as well as, diazoles, triazole, diazine and triazine compounds, and the like. Also suitable for possible use are aromatic tertiary amines, such as N,N-dimethylaniline, N,N-diethylaniline, N,N-dimethyl-p-toluidine, N-methyldiphenylamine, N,N-dimethylbenzylamine, N,N-dimethyl-1-naphthylamine, and the like. Compounds containing two or more amino groups, such as N,N,N',N'-tetramethylethylene diamine and triethylene diamine (i.e. 1,4-diazabicyclo-[2,2,2]-octane) can also be mentioned.

Preferred organic nitrogen compounds useful for scavenging the phosphorus acidic compounds present in the hydroformylation reaction product fluids of the this invention are heterocyclic compounds selected from the group consisting of diazoles, triazoles, diazines and triazines, such as those disclosed and employed herein. For example, benzimidazole and benztriazole are preferred candidates for such use.

Illustrative of suitable organic nitrogen compounds useful for scavenging the phosphorus acidic compounds include those permissible organic nitrogen compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, 1996, the pertinent portions of which are incorporated herein by reference.

The amount of organic nitrogen compound that may be present in the reaction product fluid for scavenging the phosphorus acidic compounds present in the hydroformylation reaction product fluids of the this invention is typically sufficient to provide a concentration of at least about 0.0001 moles of free organic nitrogen compound per liter of reaction product fluid. In general the ratio of organic nitrogen compound to total organophosphite ligand (whether bound with rhodium or present as free organophosphite) is at least about 0.1:1 and even more preferably at least about 0.5:1. The upper limit on the amount of organic nitrogen compound employed is governed mainly only by economical considerations. Organic nitrogen compound to organophosphite molar ratios of at least about 1:1 up to about 5:1 should be sufficient for most purpose.

It is to be understood the organic nitrogen compound employed to scavenge said phosphorus acidic compounds need not be the same as the heterocyclic nitrogen compound employed to protect the metal catalyst under harsh conditions such as exist in the aldehyde vaporizer-separator. However, if said organic nitrogen compound and said heterocyclic nitrogen compound are desired to be the same and perform both said functions in a given process, care should be taken to see that there will be a sufficient amount of the heterocyclic nitrogen compound present in the reaction medium to also provide that amount of free heterocyclic nitrogen compound in the hydroformylation process, e.g., vaporizer-separator, that will allow both desired functions to be achieved.

Accordingly the aqueous buffer solution treatment of this invention will not only remove free phosphoric acidic compounds from the metal-organophosphite ligand complex catalyst containing reaction product fluids, the aqueous buffer solution also surprisingly removes the phosphorus acidic material of the conversion product salt formed by the use of the organic nitrogen compound scavenger when employed, i.e., the phosphorus acid of said conversion product salt remains behind

in the aqueous buffer solution, while the treated reaction product fluid, along with the reactivated (free) organic nitrogen compound is returned to the hydroformylation reaction zone.

An alternate method of transferring acidity from the hydroformylation reaction product fluid to an aqueous fraction is through the intermediate use of a heterocyclic amine which has a fluorocarbon or silicone side chain of sufficient size that it is immiscible in both the hydroformylation reaction product fluid and in the aqueous fraction. The heterocyclic amine may first be contacted with the hydroformylation reaction product fluid where the acidity present in the reaction product fluid will be transferred to the nitrogen of the heterocyclic amine. This heterocyclic amine layer may then be decanted or otherwise separated from the reaction product fluid before contacting it with the aqueous fraction where it again would exist as a separate phase. The heterocyclic amine layer may then be returned to contact the hydroformylation reaction product fluid.

Another means for preventing or minimizing ligand degradation and catalyst deactivation and/or precipitation that may be useful in this invention involves carrying out the invention described and taught in copending U.S. Patent Application Serial Nos. (D-17648) and (D-17649), both filed on an even date herewith, the disclosures of which are incorporated herein by reference, which comprises using water and optionally organic nitrogen compounds as disclosed therein.

For instance, it has been found that hydrolytic decomposition and rhodium catalyst deactivation as discussed herein can be prevented or lessened by treating at least a portion of the reaction product fluid derived from the hydroformylation process and which also contains phosphorus acidic compounds formed during the hydroformylation process with water sufficient to remove at least some amount of the phosphorus acidic compounds from the reaction product fluid. Although both water and acid are factors in the hydrolysis of organophosphite ligands, it has been surprisingly discovered that

hydroformylation reaction systems are more tolerant of higher levels of water than higher levels of acid. Thus, the water can surprisingly be used to remove acid and decrease the rate of loss of organophosphite ligand by hydrolysis.

Yet another means for preventing or minimizing ligand degradation and catalyst deactivation and/or precipitation that may be useful in this invention involves carrying out the invention described and taught in copending U.S. Patent Application Serial Nos. (D-17652) and (D-17685), both filed on an even date herewith, the disclosures of which are incorporated herein by reference, which comprises using water in conjunction with acid removal substances and optionally organic nitrogen compounds as disclosed therein.

For instance, it has been found that hydrolytic decomposition and rhodium catalyst deactivation as discussed herein can be prevented or lessened by treating at least a portion of the reaction product fluid derived from the hydroformylation process and which also contains phosphorus acidic compounds formed during said hydroformylation process with water in conjunction with one or more acid removal substances, e.g., oxides, hydroxides, carbonates, bicarbonates and carboxylates of Group 2, 11 and 12 metals, sufficient to remove at least some amount of the phosphorus acidic compounds from said reaction product fluid. Because metal salt contaminants, e.g., iron, zinc, calcium salts and the like, in a hydroformylation reaction product fluid undesirably promote the self condensation of aldehydes, an advantage is that one can use the acidity removing capability of certain acid removal substances with minimal transfer of metal salts to the hydroformylation reaction product fluid.

A further means for preventing or minimizing ligand degradation and catalyst deactivation and/or precipitation that may be useful in this invention involves carrying out the invention described and taught in copending U.S. Patent Application Serial Nos. (D-17650) and (D-17651), both filed on an even date herewith, the disclosures of

which are incorporated herein by reference, which comprises using ion exchange resins and optionally organic nitrogen compounds as disclosed therein.

For instance, it has been found that hydrolytic decomposition and rhodium catalyst deactivation as discussed herein can be prevented or lessened by (a) treating in at least one scrubber zone at least a portion of said reaction product fluid derived from said hydroformylation process and which also contains phosphorus acidic compounds formed during said hydroformylation process with water sufficient to remove at least some amount of the phosphorus acidic compounds from said reaction product fluid and (b) treating in at least one ion exchange zone at least a portion of the water which contains phosphorus acidic compounds removed from said reaction product fluid with one or more ion exchange resins sufficient to remove at least some amount of the phosphorus acidic compounds from said water. Because passing a hydroformylation reaction product fluid directly through an ion exchange resin can cause rhodium precipitation on the ion exchange resin surface and pores, thereby causing process complications, an advantage is that one can use the acidity removing capability of ion exchange resins with essentially no loss of rhodium.

Other means for removing phosphorus acidic compounds from the reaction product fluids of this invention may be employed if desired. This invention is not intended to be limited in any manner by the permissible means for removing phosphorus acidic compounds from the reaction product fluids.

In addition to hydroformylation processes, other processes for which this invention may be useful include those which exhibit a loss in catalytic activity of organopolyphosphite promoted metal catalysts due to harsh reaction conditions such as employed in the separation and recovery of product from its reaction product fluid. Illustrative processes include, for example, hydroacylation (intramolecular and intermolecular), hydroamidation,

hydroesterification, carbonylation and the like. Preferred processes involve the reaction of organic compounds with carbon monoxide, or with carbon monoxide and a third reactant, e.g., hydrogen, or with hydrogen cyanide, in the presence of a catalytic amount of a metal-organopolyphosphite ligand complex catalyst. The most preferred processes include hydroformylation, hydrocyanation and carbonylation.

As with hydroformylation processes, these other processes may be asymmetric or non-asymmetric, the preferred processes being non-asymmetric, and may be conducted in any continuous or semi-continuous fashion and may involve any catalyst liquid and/or gas recycle operation desired. The particular processes for producing products from one or more reactants, as well as the reaction conditions and ingredients of the processes are not critical features of this invention. The processing techniques of this invention may correspond to any of the known processing techniques heretofore employed in conventional processes. For instance, the processes can be conducted in either the liquid or gaseous states and in a continuous, semi-continuous or batch fashion and involve a liquid recycle and/or gas recycle operation or a combination of such systems as desired. Likewise, the manner or order of addition of the reaction ingredients, catalyst and solvent are also not critical and may be accomplished in any conventional fashion.

The hydroformylation processes of this invention may be carried out using, for example, a fixed bed reactor, a fluid bed reactor, a continuous stirred tank reactor (CSTR), or a slurry reactor. The optimum size and shape of the catalysts will depend on the type of reactor used. In general, for fluid bed reactors, a small, spherical catalyst particle is preferred for easy fluidization. With fixed bed reactors, larger catalyst particles are preferred so the back pressure within the reactor is kept reasonably low. The at least one reaction zone employed in this invention may be a single vessel or may comprise two or more discrete vessels. The at least one separation

zone employed in this invention may be a single vessel or may comprise two or more discrete vessels. The at least one scrubber zone employed in this invention may be a single vessel or may comprise two or more discreet vessels. It should be understood that the reaction zone(s) and separation zone(s) employed herein may exist in the same vessel or in different vessels. For example, reactive separation techniques such as reactive distillation, reactive membrane separation and the like may occur in the reaction zone(s).

The hydroformylation processes of this invention can be conducted in a batch or continuous fashion, with recycle of unconsumed starting materials if required. The reaction can be conducted in a single reaction zone or in a plurality of reaction zones, in series or in parallel or it may be conducted batchwise or continuously in an elongated tubular zone or series of such zones. The materials of construction employed should be inert to the starting materials during the reaction and the fabrication of the equipment should be able to withstand the reaction temperatures and pressures. Means to introduce and/or adjust the quantity of starting materials or ingredients introduced batchwise or continuously into the reaction zone during the course of the reaction can be conveniently utilized in the processes especially to maintain the desired molar ratio of the starting materials. The reaction steps may be effected by the incremental addition of one of the starting materials to the other. Also, the reaction steps can be combined by the joint addition of the starting materials. When complete conversion is not desired or not obtainable, the starting materials can be separated from the product, for example by distillation, and the starting materials then recycled back into the reaction zone.

The hydroformylation processes may be conducted in either glass lined, stainless steel or similar type reaction equipment. The reaction zone may be fitted with one or more internal and/or external heat exchanger(s) in order to control undue temperature

fluctuations, or to prevent any possible "runaway" reaction temperatures.

The hydroformylation processes of this invention may be conducted in one or more steps or stages. The exact number of reaction steps or stages will be governed by the best compromise between capital costs and achieving high catalyst selectivity, activity, lifetime and ease of operability, as well as the intrinsic reactivity of the starting materials in question and the stability of the starting materials and the desired reaction product to the reaction conditions.

In an embodiment, the hydroformylation processes useful in this invention may be carried out in a multistaged reactor such as described, for example, in copending U.S. Patent Application Serial No. (D-17425-1), filed on an even date herewith, the disclosure of which is incorporated herein by reference. Such multistaged reactors can be designed with internal, physical barriers that create more than one theoretical reactive stage per vessel. In effect, it is like having a number of reactors inside a single continuous stirred tank reactor vessel. Multiple reactive stages within a single vessel is a cost effective way of using the reactor vessel volume. It significantly reduces the number of vessels that otherwise would be required to achieve the same results. Fewer vessels reduces the overall capital required and maintenance concerns with separate vessels and agitators.

For purposes of this invention, the term "hydrocarbon" is contemplated to include all permissible compounds having at least one hydrogen and one carbon atom. Such permissible compounds may also have one or more heteroatoms. In a broad aspect, the permissible hydrocarbons include acyclic (with or without heteroatoms) and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic organic compounds which can be substituted or unsubstituted.

As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds unless otherwise indicated. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, alkyl, alkyloxy, aryl, aryloxy, hydroxy, hydroxyalkyl, amino, aminoalkyl, halogen and the like in which the number of carbons can range from 1 to about 20 or more, preferably from 1 to about 12. The permissible substituents can be one or more and the same or different for appropriate organic compounds. This invention is not intended to be limited in any manner by the permissible substituents of organic compounds.

Further, an accelerated testing procedure has been devised for demonstrating the potential effectiveness of free heterocyclic nitrogen compounds for minimizing or preventing such catalytic deactivation and/or rhodium loss as discussed herein that may occur during a continuous liquid recycle hydroformylation involving the use of a rhodium-organopolyphosphite ligand complex catalyst and vaporization separation i.e., distillative recovery of the desired aldehyde product. Said testing procedure is outlined in certain of the following examples and comprises subjecting a solubilized activated rhodium-organopolyphosphite ligand complex catalyst containing reaction product fluid to harsh vaporizer type conditions for a much longer sustained period of time than would be experienced during a normal continuous liquid recycle hydroformylation process in order to obtain meaningful results in a much shorter and manageable period of time. For instance, the catalytic deactivation and/or rhodium loss as discussed herein that may occur during a continuous liquid recycle hydroformylation such may take days or weeks to define quantitatively under normal aldehyde distillative recovery procedures because the catalyst is subjected to such vaporizer conditions for only a

matter of a few minutes each day, whereas applicants accelerated test can be completed within hours by continuously maintaining the reaction product fluid at high aldehyde recovery type distillation temperatures for a prolonged period of time in the total absence of carbon monoxide.

Certain of the following examples are provided to further illustrate this invention.

The hydroformylation of propylene was conducted in a continuous single pass using glass reactors. The reactor system was equipped with various instruments so that the catalyst activity of each glass reactor could be measured and profiled as a function of time. The catalytic activity is reported in terms of hydroformylation rate/outlet propylene partial pressure, psi., wherein the hydroformylation rate in terms of gram-moles per liter of aldehyde product per hour is normalized for the propylene partial pressure. The hydroformylation process involved passing nitrogen, carbon monoxide, hydrogen and propylene through water (unless otherwise noted) and feeding the gases continuously to the reactor. The flows of the four gas feeds were maintained at roughly the same rates for all the hydroformylation experiments to assure similar feed rates to each reactor and equivalent stripping conditions. The partial pressures of the components at the outlet were determined by the activity of the catalyst. Flow rates and typical partial pressures for the hydroformylation experiments are given below.

	Feed Rate	Partial Pressure
Component	(std L/hr)	(psi)
N_2	5.6	50-70
H_2	4.7 - 4.8	40-60
CO	4.7 - 4.8	40-60
Propylene	1 - 1.2	1-6

Hydroformylation aldehyde products were stripped from the reactor with nitrogen and the unreacted gases. The composition of

the vapor leaving the reactor was determined by multiplying the outlet flow by the outlet aldehyde concentration and dividing by the reaction volume. The catalytic activity was measured by dividing the actual rate by the predicted rate. The predicted rate was based on a kinetic equation where the dependence on propylene partial pressure and rhodium concentration are assumed to be one. Thus, the catalytic activity of a freshly prepared rhodium-bisphosphite complex catalyst in the glass reactors is considered to normally line out at 100%. The isomer ratio of the normal to branched aldehyde products was obtained at the same time by gas chromatography.

Example 1

A solution containing 200 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 1.0% of Ligand D (as described above) and 4.0% benzimidazole was made up in a 5:95 % mixture of 2-ethylbutyraldehyde and tetraglyme solvent. Fifteen milliliters of this solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for one-half hour to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 100°C. After 3 days, the nitrogen purge was turned off.

The rhodium-bisphosphite complex catalyst solution so obtained was then used to catalyze the hydroformylation of propylene (without first having passed the reactant gases through water) in a stirred glass reactor at about 100°C as described above. The catalytic activity of the rhodium complex catalyst of said process was found to be about the same as that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of benzimidazole and which has not been subjected to said nitrogen treatment.

This experiment demonstrated that the bisphosphite promoted rhodium catalyst was not deactivated upon subjecting the

catalyst in the presence of benzimidazole to a high temperature in the absence of syn gas (carbon monoxide and hydrogen) for a prolong period of time.

Comparative Example A

A solution containing 200 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 1.0% of Ligand D (as described above) was made up in a 5:95 % mixture of 2-ethylbutyraldehyde and tetraglyme solvent. The solution was free of benzimidazole. Fifteen milliliters of this solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for one-half hour to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 100°C. After 3 days, the nitrogen purge was turned off.

The rhodium-bisphosphite complex catalyst solution so obtained was then used to catalyze the hydroformylation of propylene (without first having passed the reactant gases through water) in a stirred glass reactor at about 100°C as described above. The catalytic activity of the rhodium complex catalyst of said process was found to be about 10 percent of that normally obtainable under similar hydroformylation conditions by the use of a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of benzimidazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated that the bisphosphite promoted rhodium catalyst was substantially deactivated upon being subjected, in the absence of a free heterocyclic amine compound such as benzimidazole and in the absence syn gas (carbon monoxide and hydrogen) to a high temperature for a prolong period of time.

Example 2

A solution containing 200 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 2.0% of Ligand D (as described above) and 0.7% of di-2-benzimidazole was made up in tetraglyme solvent. Fifteen milliliters of this solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for one-half hour to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 100°C. After 3 days, the nitrogen purge was turned off.

The rhodium-bisphosphite complex catalyst solution so obtained was then used to catalyze the hydroformylation of propylene in a stirred glass reactor at about 100°C as described above. The catalytic activity of the rhodium complex catalyst of said process was found to be about the same as that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of di-2-benzimidazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated that the bisphosphite promoted rhodium catalyst was not deactivated upon subjecting the catalyst in the presence of di-2-benzimidazole to a high temperature in the absence of syn gas (carbon monoxide and hydrogen) for a prolong period of time.

Example 3

A solution containing 207 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 1.54% of Ligand D (as described above) and 1.0% of 1-hydroxymethylbenzimidazole was made up in tetraglyme solvent. Fifteen milliliters of this solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for 80 minutes to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 100°C. After 4 days, the nitrogen purge was turned off.

The rhodium-bisphosphite complex solution so obtained was then used to catalyze the hydroformylation of propylene in a stirred glass reactor at about 100°C as described above. The catalytic activity of the rhodium complex catalyst of said process was found to be about the same as that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of 1-hydroxymethylbenzimidazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated that the bisphosphite promoted rhodium catalyst was not deactivated upon subjecting the catalyst in the presence of 1-hydroxymethylbenzimidazole to a high temperature in the absence of syn gas (carbon monoxide and hydrogen) for a prolong period of time.

Example 4

A solution containing 200 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 2.0% of Ligand D (as described above) and 0.7% of 1-methyl-2-phenylbenzimidazole was made up in tetraglyme solvent. The solution was free of benzimidazole. Fifteen milliliters of this solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for one-half hour to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 100°C. After 3 days, the nitrogen purge was turned off.

The rhodium-bisphosphite complex catalyst solution so obtained was then used to catalyze the hydroformylation of propylene in a stirred glass reactor at about 100°C as described above. The catalytic activity of the rhodium complex catalyst of said process was found to be about 10 percent of that normally obtainable under similar hydroformylation conditions by the use of a freshly prepared rhodium-

bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of 1-methyl-2-phenylbenzimidazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated that the bisphosphite promoted rhodium catalyst was substantially deactivated upon being subjected in the presence of 1-methyl-2-phenylbenzimidazole, and in the absence of syn gas (carbon monoxide and hydrogen) at a high temperature for a prolonged period of time.

Example 5

A solution containing 200 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 2.0% of Ligand D (as described above) and 1.0% of 2-methylbenzimidazole was made up in a 50:50% mixture of dodecylaldehyde and tetraglyme solvent. Fifteen milliliters of this solution was charged into the reactor. A stream of nitrogen was passed through the solution while the reactor was maintained at 100°C. After 5 days, the nitrogen purge was turned off.

The rhodium-bisphosphite complex solution so obtained was then used to catalyze the hydroformylation of propylene in a stirred glass reactor at about 100°C as described above. The catalytic activity of the rhodium complex catalyst of said process was found to be about the same as that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of 2-methyl-benzimidazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated that the bisphosphite promoted rhodium catalyst was not deactivated upon subjecting the catalyst in the presence of 2-methyl-benzimidazole to a high

temperature in the absence of syn gas (carbon monoxide and hydrogen) for a prolong period of time.

Comparative Example C

A solution containing 200 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 2.0% of Ligand D (as described above) was made up in a 50:50% mixture of dodecylaldehyde and tetraglyme solvent. The solution was free of 2-methylbenzimidazole. Fifteen milliliters of this solution was charged into the reactor. A stream of nitrogen was then passed through the solution while the reactor was maintained at 100°C. After 5 days, the nitrogen purge was turned off.

The rhodium-bisphosphite complex solution so obtained was then used to catalyze the hydroformylation of propylene in a stirred glass reactor at about 100°C as described above. The catalytic activity of the rhodium complex catalyst of said process was found to be about 50 percent of that normally obtainable under similar hydroformylation conditions by the use of a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of 2-methylbenzimidazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated that the bisphosphite promoted rhodium catalyst substantially deactivates in the absence of 2-methylbenzimidazole and in the absence of a hydroformylation amount of syn gas (carbon monoxide and hydrogen) when subjected to a high temperature for a prolong period of time.

Example 6

A solution containing 250 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 1.0% of Ligand D (as described above) and 0.5% benzimidazole was made up in a 5:95% mixture of 2-ethylbutyraldehyde and tetraglyme solvent. Fifteen milliliters of this

solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for one-half hour to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 125°C. After 1 day the nitrogen purge was turned off.

The rhodium-bisphosphite complex catalyst solution so obtained was then used to catalyze the hydroformylation of propylene (on day one the reactant gases were not passed through water, but were thereafter) in a stirred glass reactor at about 125°C as described above. After 5 days the catalytic activity of the rhodium complex catalyst of said process was found to increase from about 10 to 20 percent of that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of benzimidazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated a catalytic activity result that was about five times higher than that obtained by a controlled experiment that was carried out in essentially the same manner but in the absence of any benzimidazole.

Comparative Example D

In a controlled experiment the catalytic activity of the fresh rhodium complex catalyst after having been subjected to nitrogen at 125°C for 1 day as described above, was found to be only about 4 percent (after 5 days of hydroformylation) of that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of benzimidazole and which had not been subjected to said nitrogen treatment.

Example 7

A solution containing 250 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 1.0% of Ligand D (as described above) and 2.0% of benzimidazole was made up in a 5:95% mixture of 2-ethylbutyraldehyde and tetraglyme solvent. Fifteen milliliters of this solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for one-half hour to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 125°C. After 1 day the nitrogen purge was turned off.

The rhodium-bisphosphite complex catalyst solution so obtained was then used to catalyze the hydroformylation of propylene (during the first day the reactant gases were not passed through water, but were thereafter) in a stirred glass reactor at about 125°C as described above. After 5 days the catalytic activity of the rhodium complex catalyst of said process was found to be about 10 percent of that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of benzimidazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated a catalytic activity result that was substantially higher than the 4 percent obtained under similar hydroformylation conditions by the use the rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of benzimidazole and which had been subjected to said nitrogen treatment as described in the control experiment of Example 5 above.

Example 8

A solution containing 250 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 1.0% of Ligand D (as described above) and 0.25% of pyrazole was made up in a 5:95% mixture of 2-ethylbutyraldehyde and tetraglyme solvent. Fifteen milliliters of this

solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for one-half hour to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 110°C. After 3 days the nitrogen purge was turned off.

The rhodium-bisphosphite complex catalyst solution so obtained was then used to catalyze the hydroformylation of propylene (during the first 3 days the reactant gases were not passed through water, but were thereafter) in a stirred glass reactor at about 110°C as described above. After 5 days the catalytic activity of the rhodium complex catalyst of said process was found to be about 7 percent of that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of pyrazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated a catalytic activity result that was substantially higher than the 4 percent obtained under similar hydroformylation conditions by the use the rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of pyrazole and which had been subjected to said nitrogen treatment as described in the control experiment of Example 5 above.

Example 9

This example demonstrates the ability of benzimidazole in keeping rhodium in solution in the absence of syn gas (carbon monoxide and hydrogen).

A solution containing 800 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate and 2.0% Ligand D (as described above) was made up in a 1:1 mixture of n-valeraldehyde and tetraglyme solvent. Twenty five milliliters of this solution was then charged into a Fisher-Porter bottle. The bottle was then pressurized

with syn gas (carbon monoxide and hydrogen) and heated at 80°C for 30 minutes to form a homogenous solution. After being cooled to room temperature, 5 milliliters of the solution was charged into each of two glass tubes equipped with a fretted-glass gas purger. To one of the solutions, 0.1 grams of benzimidazole was added. The solutions were then purged with nitrogen wile being heated at 100°C. Within 60 minutes, a gray precipitate formed in the tube of the solution without the benzimidazole. The solution in the tube containing the benzimidazole remained clear for 4 days at 100°C.

Said experiment demonstrates that the presence of benzimidazole in the catalyst solution prevented the rhodium from precipitating out of solution.

Example 10

A solution containing 207 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 1.54% of Ligand D (as described above) and 1.0% of benzotriazole was made up in tetraglyme solvent. Fifteen milliliters of this solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for 80 minutes to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 100°C. After 3 days, the nitrogen purge was turned off.

The rhodium-bisphosphite complex catalyst solution so obtained was then used to catalyze the hydroformylation of propylene in a stirred glass reactor as described above. The catalytic activity of the rhodium complex catalyst of said process was found to be about the same as that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of benzotriazole and which had not been subjected to said nitrogen treatment.

This experiment demonstrated that the bisphosphite promoted rhodium catalyst was not deactivated upon subjecting the catalyst in the presence of benzotriazole to a high temperature in the absence of syn gas (carbon monoxide and hydrogen) for a prolong period of time.

Comparative Example E

A solution containing 200 ppm of rhodium in the form of rhodium dicarbonyl acetylacetonate, 2.0% of Ligand D (as described above) and 2.0% of 1,4-diazobicyclo[2,2,2]octane was made up in tetraglyme solvent. Fifteen milliliters of this solution was charged into the reactor and exposed to syn gas ($CO:H_2$) for 80 minutes to form the catalyst complex. A stream of nitrogen was then passed through the solution while the reactor was maintained at 125°C. After 1 day the nitrogen purge was turned off.

The rhodium-bisphosphite complex solution so obtained was then used to catalyze the hydroformylation of propylene in a stirred glass reactor at about 100°C as described above. After 2 days the catalytic activity of the rhodium complex catalyst of said process was found to be about 4 percent of that normally obtainable under similar hydroformylation conditions by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of 1,4-diazobicyclo[2,2,2]octane and which had not been subjected to said nitrogen treatment.

This experiment demonstrated a catalytic activity result that was about the same as that obtained by the use a freshly prepared rhodium-bisphosphite complex catalyst derived from rhodium dicarbonyl acetylacetonate and Ligand D in the absence of 1,4-diazobicyclo[2,2,2]octane under similar hydroformylation conditions after having been subjected to nitrogen at 125°C for 1 day as described in the control experiment of Comparative Example D above.

Examples 11 to 15 illustrate the in situ buffering effect of nitrogen containing additives such as benzimidazole and the ability of these additives to transfer the acidity to an aqueous buffer solution.

Example 11

This control example illustrates the stability of Ligand D (as identified herein) in a solution containing 200 parts per million of rhodium, and 0.39 percent by weight of Ligand D in butyraldehyde containing aldehyde dimer and trimer in the absence of added acid or benzimidazole.

To a clean, dry 25 milliliter vial was added 12 grams of the butyraldehyde solution mentioned above. Samples were analyzed for Ligand D using High Performance Liquid Chromatography after 24 and 72 hours. The weight percent of Ligand D was determined by High Performance Liquid Chromatography relative to a calibration curve. No change in the concentration of Ligand D was observed after either 24 or 72 hours.

Example 12

This Example is similar to Example 11 except that phosphorus acid was added to simulate the type of acid that might be formed during hydrolysis of an organophosphite.

The procedure for Example 11 was repeated with the modification of adding 0.017grams of phosphorous acid (H_3PO_3) to the 12 gram solution. After 24 hours the concentration of Ligand D had decreased from 0.39 to 0.12 percent by weight; after 72 hours the concentration of Ligand D had decreased to 0.04 percent by weight. This data shows that strong acids catalyze the decomposition of Ligand D.

Example 13

This Example is similar to Example 11 except that both phosphorus acid and benzimidazole were added.

The procedure for Example 11 was repeated with the modification of adding 0.018 grams of phosphorous acid and 0.0337 grams of benzimidazole to the solution. No decomposition of Ligand D was observed after either 24 or 72 hours. This shows that the addition of benzimidazole effectively buffers the effect of the strong acid and thereby prevents the rapid decomposition of Ligand D.

Example 14

This example shows that an aqueous buffer can recover the acidity from the nitrogen base in situ buffer and allow the nitrogen base to partition into the organic phase, where it can be recycled to the hydroformylation zone.

Solid (benzimidazole)(H_3PO_4) was prepared by placing 1.18 grams (10 mmole) of benzimidazole in a 250 milliliter beaker and dissolving the benzimidazole in 30 milliliters of tetrahydrofuran. To this solution was slowly added 0.5 grams of 86 percent by weight of phosphoric acid (H_3PO_4). Upon addition of the acid a precipitate formed. The precipitate was collected on a sintered glass frit and washed with tetrahydrofuran. The resulting solid was air-dried with the application of vacuum and used without any further purification. 0.109 grams (0.504 mmole) of the water-soluble (benzimidazole)(H_3PO_4) solid prepared in the previous step was dissolved in 10 grams of 0.1 M pH 7 sodium phosphate buffer solution. The resulting solution was extracted with 10 grams of valeraldehyde. The organic layer was then separated from the aqueous layer using a separatory funnel. The volatile components were then removed from the organic layer by distillation at 100°C to yield a solid. The solid was identical to authentic benzimidazole as shown by thin layer chromatography utilizing a 1:1 by volume mixture of chloroform and acetone as the eluent and silica as the stationary phase. Based on

recovery of the solid, benzimidazole was completely transferred to the organic phase.

This data shows that an organic soluble nitrogen base which exists as a strong acid salt can be regenerated by contact with an aqueous buffer and returned to the organic phase.

Example 15

This example shows that a buffer solution is effective at neutralizing an organic soluble salt of a weak base and strong acid thus allowing the base to return to the organic phase and effectively removing the acid from the organic phase.

A butyraldehyde solution was prepared containing 1.0 percent by weight of benzotriazole. The solution was then analyzed by Gas Chromatography for benzotriazole content to serve as a reference sample. To the solution prepared in the previous step was added 0.25 mole equivalents of phosphorous acid (H_3PO_3). In a one pint glass bottle was added 50 grams of the butyraldehyde solution containing benzotriazole and 50 grams of a pH 7, 0.2 molar sodium phosphate buffer solution. The mixture was stirred for 15 minutes and then transferred to a separatory funnel. The aqueous layer was then separated from the aldehyde layer. The aqueous layer was analyzed for H_3PO_3 content by Ion Chromatography. The aldehyde layer was analyzed for benzotriazole content by Gas Chromatography and H_3PO_3 content by Ion Chromatography. The H_3PO_3 was found to be completely transferred into the aqueous layer. Complete return of benzotriazole to the butyraldehyde layer was also found.

This data shows that an organic soluble salt of a weak base and strong acid can be completely neutralized by contacting the organic phase with an aqueous buffer solution and that the free base is thereby returned to the organic phase.

Although the invention has been illustrated by certain of the preceding examples, it is not to be construed as being limited thereby; but rather, the invention encompasses the generic area as hereinbefore disclosed. Various modifications and embodiments can be made without departing from the spirit and scope thereof.

Claims

1. A method of stabilizing a metal-organopolyphosphite ligand complex catalyst against deactivation in a process which comprises reacting one or more reactants in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more products, which method comprises conducting said process in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, wherein said one or more free heterocyclic nitrogen compounds are selected from the group consisting of diazoles, triazoles, diazines and triazines.

2. The method of claim 1 comprising stabilizing a metal-organopolyphosphite ligand complex catalyst against deactivation in a process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, which method comprises conducting said process in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, wherein said one or more free heterocyclic nitrogen compounds are selected from the group consisting of diazoles, triazoles, diazines and triazines.

3. A hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free

organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, and in which at least a portion of said hydroformylation process is conducted under conditions sufficient to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, wherein said hydroformylation process is conducted in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, and wherein said one or more free heterocyclic nitrogen compounds are selected from the group consisting of diazoles, triazoles, diazines and triazines.

4. A continuous liquid recycle hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, and in which at least a portion of said process is conducted under vaporization separation conditions sufficient to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, wherein said process is conducted in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, and wherein said one or more free heterocyclic nitrogen compounds are selected from the group consisting of diazoles, triazoles, diazines and triazines.

5. The process of claim 3 comprising an improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid

comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, and wherein at least a portion of said process is conducted at a carbon monoxide partial pressure sufficiently low to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, the improvement comprising conducting said process in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, wherein said one or more free heterocyclic nitrogen compounds are selected from the group consisting of diazoles, triazoles, diazines and triazines.

6. The process of claim 4 comprising an improved continuous liquid recycle hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone by vaporization separation the one or more aldehydes from said reaction product fluid, and wherein said vaporization separation is conducted at a carbon monoxide partial pressure sufficiently low to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, the improvement comprising conducting said vaporization separation in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, wherein said one or more free heterocyclic nitrogen compounds are selected from the group consisting of diazoles, triazoles, diazines and triazines.

7. The process of claim 1 which comprises a hydroformylation, hydroacylation (intramolecular and intermolecular), hydroamidation, hydroesterification or carbonylation process.

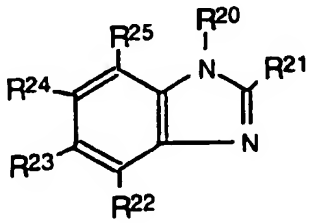
8. The processes of claims 1, 2, 3, 4, 5 and 6 wherein the one or more free heterocyclic nitrogen compounds comprises one or more diazoles selected from the group consisting of imidazoles, pyrazoles and indazoles.

9. The processes of claims 1, 2, 3, 4, 5 and 6 wherein the one or more free heterocyclic nitrogen compounds comprises one or more triazoles selected from the group consisting of 1,3,3-triazoles, 1,2,4-triazoles, 2,1,3-triazoles and 4,1,2-triazoles.

10. The processes of claims 1, 2, 3, 4, 5 and 6 wherein the one or more free heterocyclic nitrogen compounds comprises one or more diazines selected from the group consisting of 1,2-diazines, 1,3-diazines and 1,4-diazines.

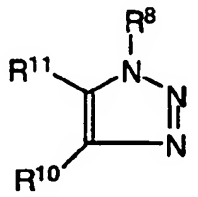
11. The processes of claim 8 wherein the diazole is a benzimidazole.

12. The processes of claim 11 wherein the benzimidazole is represented by the formula:



wherein R^{20}, R^{21}, R^{22}, R^{23}, R^{24} and R^{25} are identical or different and each represent a hydrogen atom or a monovalent substituent, with the proviso that R^{20} and R^{21} are not both monovalent hydrocarbon radicals at the same time.

13. The processes of claim 9 wherein the triazole is represented by the formula:

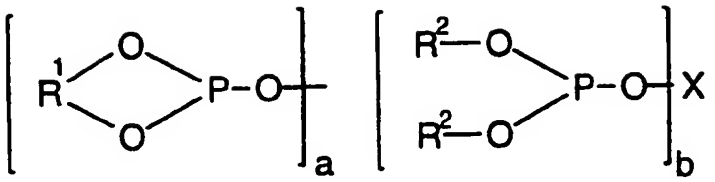


wherein R^8, R^{10} and R^{11} are identical or different and each represents a hydrogen atom or a monovalent substituent, and adjacent substituents R^8 and R^{11}, or R^{10} and R^{11}, may optionally be taken together to form a substituted or unsubstituted divalent radical which together with the two atoms of the formula to which said adjacent substituents are bonded form a cyclic ring.

14. The processes of claim 13 wherein the triazole is benzotriazole.

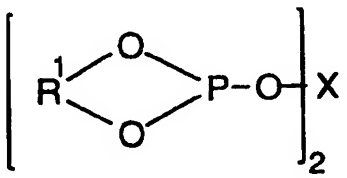
15. The processes of claims 1, 2, 3, 4, 5 and 6 wherein said metal-organopolyphosphite ligand complex catalyst is homogeneous or heterogeneous.

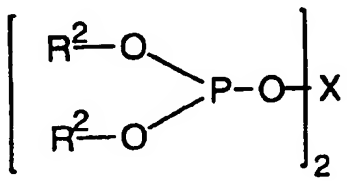
16. The processes of claims 1, 2, 3, 4, 5 and 6 wherein said metal-organopolyphosphite ligand complex catalyst comprises rhodium complexed with an organopolyphosphite ligand represented by the formula:

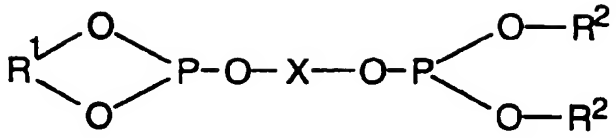


wherein X represents a substituted or unsubstituted n-valent organic bridging radical containing from 2 to 40 carbon atoms, each R^1 is the same or different and represents a divalent organic radical containing from 4 to 40 carbon atoms, each R^2 is the same or different and represents a substituted or unsubstituted monovalent hydrocarbon radical containing from 1 to 24 carbon atoms, wherein a and b can be the same or different and each have a value of 0 to 6, with the proviso that the sum of a + b is 2 to 6 and n equals a + b.

17. The processes of claim 16 wherein said metal-organopolyphosphite ligand complex catalyst comprises rhodium complexed with an organopolyphosphite ligand having the formula selected from:







wherein X represents a substituted or unsubstituted divalent hydrocarbon bridging radical containing from 2 to 40 carbon atoms, each R^1 is the same or different and represents a divalent hydrocarbon radical containing from 4 to 40 carbon atoms, and each R^2 is the same or different and represents a substituted or unsubstituted monovalent hydrocarbon radical containing from 1 to 24 carbon atoms.

18. The processes of claims 2, 3, 4, 5 and 6 wherein at carbon monoxide partial pressures sufficiently low to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst, the one or more free heterocyclic nitrogen compounds (i) have a coordination strength with respect to the metal of said metal-organopolyphosphite ligand complex catalyst sufficient to compete with carbon monoxide to effect at least some coordination with the metal of said metal-organopolyphosphite ligand complex catalyst, and (ii) have a coordination strength with respect to the metal of said metal-organopolyphosphite ligand complex catalyst sufficient not to compete with coordination of the organopolyphosphite ligand with the metal of said metal-organopolyphosphite ligand complex catalyst.

19. The processes of claims 2, 3, 4, 5 and 6 wherein at carbon monoxide partial pressures sufficiently low to effect at least some deactivation of the metal-organopolyphosphite ligand complex catalyst the one or more free heterocyclic nitrogen compounds (i) have a coordination strength with respect to the metal of said metal-organopolyphosphite ligand complex catalyst sufficient to effect at least some coordination with the metal of said metal-organopolyphosphite

ligand complex catalyst, and (ii) have a coordination strength with respect to the metal of said metal-organopolyphosphite ligand complex catalyst less than the organopolyphosphite ligand of said metal-organopolyphosphite ligand complex catalyst.

20. The processes of claims 1, 2, 3, 4, 5 and 6 wherein said reaction product fluid contains phosphorus acidic compounds, at least a portion of which are scavenged by said one or more free heterocyclic nitrogen compounds.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 96/19410

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C45/50 C07F9/02 B01J31/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C C07F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 149 894 A (DAVY MCKEE LONDON) 31 July 1985 see page 23; claims -----	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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1

Date of the actual completion of the international search	Date of mailing of the international search report
6 March 1997	12.03.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/US 96/19410

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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